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THE CHEMICAL CONVERSION OF SOLID WASTES TO USEFUL PRODUCTS

OREGON STATE UNIVERSITY

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ENVIRONMENTAL PROTECTION AGENCY

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16. ABSTRACT

The use of solid wastes as raw materials for the production of useful products depends primarily on the successful application of chemical and engineering technology to waste disposal problems. The objectives of this study were to: (1) identify the chemical nature of the constituent of solid wastes, (2) investigate transformation process, and (3) conduct engineering and economic evaluation of pilot plant operations. The results of this study will be useful in the development of a solid waste chemical transformation facility, which will be capable of recovering waste generated from municipal, commercial, and agricultural sources for reutilization processes. This report was designed to provide the impetus for continued studies on reutilization processes rather than the culmination of a research effort.

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

As part of these activities, this study describes the use of solid wastes as raw materials for producing useful products through the application of chemical and engineering technology.

A. W. Breidenbach, Ph.D.
Director
National Environmental
Research Center, Cincinnati

TABLE OF CONTENTS

Subject Page

Introduction 1

Chemical Nature of The Constituents of Solid Wastes............ 2

Composition... 2

Municipal Refuse.................................... 2
Industrial Wastes................................... 3
Agricultural Residues............................... 3
Glass... 4
Plastics.. 4
References.. 22
Tables
II. B. 1. Composition of Typical Municipal Refuse as Reported by Kaiser..................... 25
II. B. 2. Composition of Municipal Refuse Collected in Various States as Reported by Hickman... 26
II. B. 3. Industrial Wastes by Categories........... 27
II. B. 4. Estimate of Industrial Waste Composition in Oregon..................... 28
II. B. 5. Composition of Poultry Manures............ 29
II. B. 6. Composition of Manures of Different Animals.......................... 29
II. B. 7. Composition of Cereal Straws.............. 30
II. B. 8. Composition of Grass Seed Straws.......... 31
II. B. 9. Composition of Some Typical Glasses....... 32
II. B. 10. Production and Sales of Plastics in 1970... 33

Chemical Nature of Constituents........................... 34

Cellulose... 34
Plastics.. 35
References.. 37
Figure
II. C. 1. Schematic Diagram of The Cellulose Molecule................................. 39
Tables
II. C. 1. Products of Thermal Decomposition of Cellulose............................ 40
II. C. 2. Cellulose Derivatives and Their Uses....... 41
II. C. 3. Solubility of Some Plastics in Selected Solvents.......................... 42
II. C. 4. Effect of Acids and Bases on Certain Plastics................................. 43

Subject Page

Chemical Processes 44

Crosslinking 44

Chemistry 45
Process 49
Experimental Results 52
References 57

Figures

III. B. 1. Schematic Diagram for Straw Particleboard Formation 59
III. B. 2. Effect of Wax Removal on Straw Particleboard Physical Properties 60
III. B. 3. Increased Board Strength Brought About by Increased Density 61
III. B. 4. Effect of Pressing Time on Modulus of Rupture 62
III. B. 5. Increased Board Strength Caused by Increased Resin Concentration 63
III. B. 6. Relationship Between Density and Thermal Conductivity 64
III. B. 7. The Relationship Between Pressure and Density 65
III. B. 8. Showing the Influence of Density on The Modulus of Elasticity 66

Tables

III. B. 1. Thermal Conductivity of Straw Particleboard and Other Substances 67
III. B. 2. Physical Properties of Straw Particleboard 68
III. B. 3. Changes in Weight and Linear Dimension of Boards Made From Various Materials When Soaked in Water for 24 Hours 69

Nitrogen and Phosphorus Enrichment 70

Chemistry 70
Process 73
Experimental Results 75
References 80

Figures

III. C. 1. Schematic Diagram of The Nitrogen-Phosphorus Enrichment Process 81
III. C. 2. The Effect of Reaction Time on Nitrogen Fixation in the Reaction of Cellulose and Urea 82

Subject Page

Figures
III. C. 3. Effect of Reaction Temperature on Nitrogen Concentration.................... 83
III. C. 4. Effect of Reactant Concentration on Nitrogen Concentration.................... 84
III. C. 5. Effect of Catalyst Concentration on Nitrogen Concentration................. 85
III. C. 6. Effect of Reaction Time on Phosphorus Concentration.................. 86
III. C. 7. Effect of Reaction Temperature on Phosphorus Concentration.................. 86
III. C. 8. Effect of Reactant Concentration on Phosphorus Concentration.................. 87
Tables
III. C. 1. Soil Test With Amino Cellulose............ 88
III. C. 2. Phosphorylation of Straw.................. 89
III. C. 3. Nitrogen and Phosphorus Enrichment of Straw................................ 90
III. C. 4. Soil Test With N-Enriched Paper........... 91
III. C. 5. Soil Test With N and P Enriched Paper..... 92

Acetylation of Wastes.................................. 93

Chemistry... 93
Process... 95
Experimental Results.................................... 97
References.. 102
Figures
III. D. 1. Schematic of Vapor Phase Acetylation of Solid Wastes.......................... 103
III. D. 2. Schematic of The Fiber Process of Acetylation of Solid Wastes............... 104
III. D. 3. Schematic Diagram of The Solution Process for Acetylation of Solid Waste.... 105
III. D. 4. Effect of Reaction Time on The Degree of Acetylation..................... 106
III. D. 5. Effect of Reaction Time, from 1 to 10 Minutes, on Degree of Acetylation......... 107
III. D. 6. Effect of Anhydride Concentration on Acetyl Content........................... 108
III. D. 7. Showing The Realtionship Between Catalyst and Degree of Acetylation When Using Perchloric Acid............... 109

Hydrogenation of Wastes................................ 110

Chemistry... 110

Subject Page

Experimental Results 113
References 119

Figures

III. E. 1. Gas Train for Analysis of The Head Gas from the High Pressure Reaction Apparatus 126
III. E. 2. Carbon Monoxide Analysis System 127
III. E. 3. Gas Chromatographic - Mass Spectrometric Analysis System 127

Tables

III. E. 1. Reaction Conditions and Products of Hydrogenations 128
III. E. 2. Showing the Amounts, in Grams, of Solid Residue, Oil and Water Produced per Gram of Cellulose Hydrogenated 129
III. E. 3. Information From Standard Oil Company Concerning A Sample of Oil From The Hydrogenation of Waste 130
III. E. 4. Showing the Crudely Determined Material Balance of The Hydrogenation Reactions 131

Etherification 132

Chemistry 132
Experimental Results 133
Discussion 133
References 134

Table

III. F. 1. Some Properties of Methyl and Ethyl Ethers of Cellulose 135

Oxidation of Cellulose 136

Chemistry 138
Experimental Results 141
Discussion 142
References 144

Figure

III. G. 1. Showing the Oxygen Comsumption with Time in The Chromic Acid Oxidation of Filter Paper 148

Tables

III. G. 1. Periodate Oxidation 149
III. G. 2. Persulfate Oxidation 150
III. G. 3. Chromic Acid Oxidation 150

Pulping of Straw 151

Subject Page

Chemistry.. 151
Disucssion... 152
References... 153

Figure

III. H. 1. Showing The Reduced Yield with Increased Acid Concentration During Nitric Acid Pulping............................. 154

Tables

III. H. 1. Nitric Acid Pulping of Annual Ryegrass Straw.................................... 155
III. H. 2. Sodium Hydroxide Pulping of Straw......... 155

Pilot Plant Studies.................................... 156

Economic and Engineering Analysis...................... 156

Crosslinking... 156
References... 162

Figures

IV. B. 1. Block Diagram Showing The Particleboard Process.................................... 163
IV. B. 2. Schematic Diagram Showing The Straw Particleboard Process................ 164

Tables

IV. B. 1. Resins Used in The Laboratory Study of Straw Particleboard..................... 165
IV. B. 2. Estimation of Fixed-Capital Investment Cost........................... 166
IV. B. 3. Estimation of Total Product Cost........... 167

THE CHEMICAL CONVERSION
OF SOLID WASTES
TO USEFUL PRODUCTS

In recent years, the problems associated with solid waste disposal have become a national crisis. This situation has developed because increasing amounts of wastes are being produced each year and present waste management techniques are not adequate to prevent serious environmental pollution. More wastes are being produced because 1) our population is increasing and 2) because our per capita rate of waste generation is also increasing. In 1920, the per capita production of municipal, commercial and industrial solid wastes was 2.0 pounds per day. By 1969 this figure had risen to 5.3 pounds per person per day. During this same period of time, the population of the United States had increased from 106 million to 200 million. When agricultural wastes are added, the figures become higher yet. A study in California reveals that an estimated 70 million tons of solid municipal, industrial and agricultural wastes were generated in 1967, an average of 20.2 pound per capita per day. Agricultural residues account for 48.8% of this total, while municipal refuse accounts for 32.0% and the industrial wastes account for 19.2%.

Over 80% of the solid wastes produced in the nation are disposed of by open dumping, landfilling, or sanitary landfilling, while about 10% are incinerated, and the rest are composted, dumped at sea, or disposed of in other ways.

Although ocean dumping is practiced by many cities located near the ocean, its practice is being discouraged because of problems associated with floating debris and destruction of sea life. Several composting processes have been developed which are capable of converting municipal refuse to compost, but this technique of waste disposal has not been successfully adopted because no market for the product has developed.

Incineration is limited to those components of waste which are combustible, however, this process can lead to severe air pollution. The cost of incineration is high, partly because of the need for air pollution control equipment.

Landfilling costs are primarily determined by the haul distance and cost of the land. Leaching from a landfill can pollute surface and subsurface water, while anaerobic degradation produces methane gas.

Although none of these management techniques are entirely satisfactory, at present there is no alternative. One possible alternative is the utilization of solid wastes as raw materials for the manufacture of useful products. This technique would not only reduce the amount of waste needing disposal, but would conserve our natural resources.

The use of solid wastes as raw materials for the production of useful products will depend primarily on the successful application of chemical and engineering technology to waste disposal problems. The objectives of this study are to 1) identify the chemical nature of the constitutents of solid wastes, 2) investigate transformation processes, and 3) conduct engineering and economic evaluations of pilot plant operations. The results of this study will be useful in the development of a Solid Waste Chemical Transformation Facility, which will be capable of receiving the wastes produced in a community and disposing of them in an acceptable way.

This report is divided into three sections: Component Chemistry, Chemical Processing and Pilot Plant Studies. It contains detailed information about a few, but does not include an exhaustive evaluation of all wastes or processes known in this country. This report is designed to be the foundation for continued study of reutilization processes rather than the culmination of a research effort.

THE CHEMICAL NATURE OF THE CONSTITUENTS OF SOLID WASTES

Composition

Municipal refuse: Municipal refuse is composed of a vast array of products which have lost their usefulness and have been discarded. These wastes include home wastes, commercial wastes and city wastes. While home and commercial wastes are usually placed in a receptable for periodic removal by a collection agency to a landfill or incinerator, city wastes usually collect elsewhere and require special handling and disposal.

Home wastes include such diverse products as glass bottles, cans, plastic toys, cellophane, paper, cardboard, nails, small appliances, tools, light bulbs, clothes, rubber products, wood, and food items. If these products are not separated into classes such as metal, glass, paper, etc., in the home, this waste becomes very heterogenous.

Commercial wastes are generated by retail business and institutions such as hospitals, banks and schools. Although these wastes are also heterogenous, they contain high percentages of office waste and packaging materials.

City wastes include automobile bodies, large appliances, tires, dead animals, demolition wastes, street sweepings, crankcase oil and sewage sludge.

The composition of a sample of municipal refuse reported by Kaiser (13), is given in Table II. B. 1. Hickman (8) studied the composition of municipal refuse from different states to determine if any wide variations occur because of geographical location. His results are listed in Table II. B. 2. Paper and paper products make up the largest single category of these samples of wastes.

Industrial wastes: Industrial wastes include anything that is produced by an industrial operation that is not salvaged, sold as a by-product, or used by another industry as a raw material. Since industrial firms are designed to prepare specific products from raw materials, the wastes generated by each industry will vary depending on the nature of the product and the process.

The Oregon State Board of Health (22) recently surveyed the industries operating in Oregon to determine the types of wastes that were being produced. Table II. B. 3. lists the types of wastes being discarded and Table II. B. 4. lists the percent by volume being discarded by each industry. Paper, wood and metals are the most common types of industrial solid waste being discarded.

Agricultural residues: Agricultural residues include both animal and crop wastes. Since these wastes come from a wide variety of animals and crops, no attempt has been made to include a comprehensive list of animal and crop waste composition, however, representative data from the literature is included.

Animal wastes Current annual production of animal wastes exceeds that from any other section of the agricultural-industrial-domestic complex, with about one-half of the 1.8 billion tons produced annually being generated in confinement or feeding systems (3).

Although historically, animal wastes have been recycled through the soil, the advent of inexpensive chemical fertilizers and increased labor costs have made waste utilization uneconomical. Consequently, wastes from feed lot operations contribute to problems involving odors, insects, dust, rodents, stream pollution, nitrification of surface and ground water resources and eutrophication of surface waters.

The composition of a sample of poultry manure is given in Table II. B. 5. (31), while a comparison of the fertilizing values of a variety of manures is given in Table II. B. 6. (2). Animal manures are characterized by a high percentage of water and a significant concentration of plant nutrients.

Crop wastes Straw is a solid waste of the cereal and grass seed industries. While it is tilled into the soil in many areas, some crops, notably perennials and some soils with a high clay content prohibit the use of this practice. In some regions, open field burning has been practiced to sanitize the field and dispose of the straw, however, this practice contributes to air pollution. The primary obstacle to industrial utilization of straw is the cost of harvesting and storing the straw for year around availability.

The exact composition of straw depends on a number of factors such as type, age and climate, but the general composition of most straw is similar. Rice straw is one notable exception, in that it contains over twice as much ash as most other straws. The composition of some cereal straws is listed in Table II. B. 7. (19), and the composition of some grass seed straws is listed in Table II. B. 8. (29). One can see that cellulose, lignins and pentosans are the major components of straw.

Glass: Glass products are found in municipal and industrial refuse and present two problems for waste utilization processes. In milling operations, glass is very abrasive and can cause excessive wear in metal parts. One hospital, in Salem, Oregon, now separates glass products prior to hydropulping their wastes because excessive wear on the impeller had made their disposal process uneconomical. A second problem encountered in chemical processing of wastes, is the chemical stability of glass. If glass is separated and collected in a concentrated form, what are the problems involved in its reuse in the glass industry?

Recent emphasis has been placed on the possibility of recycling glass, and collection and delivery systems have been developed in order to provide the glass industry with a supply of discarded glass. Although the technology may be available for the reutilization of some glass, one major problem persists: the variations in glass composition. Each different type of glass, with its unique composition, has its own uses. Since physical and optical properties are determined by composition, a heterogeneous mixture of glass may have limited value in a glass recycling process.

The compositions of several types of glass are listed in Table II. B. 9. (16). These types are used for such diverse products as windows, bottles, glasses, vacuum tubes, cookware, chemical apparatus, and safety glass.

Colored glass contains small amounts of metals or metal oxides not listed in Table II. B. 9. Rose colored window glass has been produced by the addition of gold to the melt, yellow-green glass used for metal sealing is produced by the addition or uranium oxide, deep blue glass is produced by the use of cobalt oxide, and green colored fruit jars are produced by use of iron oxide.

The trade name of a glass is not indicative of its composition, since nearly 150 different compositions of glass have been marketed under the trade name of "Pyrex."

Plastics: It has been estimated that plastics make up only 1.3% of the total annual waste produced in the U.S., however, the plastics industry is growing. Plastics present a special problem to waste disposal processes, in that they do not readily decompose in landfills, and some contribute to air pollution from incineration. It is therefore felt that a review of the chemical composition of plastics will be helpful in considering the affect that plastics will have on chemical processes.

Plastics are polymers which can be molded or shaped. Polymers are long chain molecules formed by the bonding of smaller molecular units called monomers:

$$\underset{\text{monomer}}{n\,A} \longrightarrow \underset{\text{Polymer}}{[A]_n}$$

If all of the molecules making up the polymers are the same, it is called a homopolymer, but if two different molecules are used to make the polymer, it is called a copolymer:

$$\underset{\text{monomer}}{n\,A + n\,B} \longrightarrow \underset{\text{Polymer}}{[A - B]_n}$$

Some polymers are formed by condensation (15:39), that is, a small molecule is eliminated as the monomer reacts to form the polymer:

$$n\,HO - A - OH \longrightarrow H[O - A]_n\,OH + (n - 1)H_2O$$

Many plastics are formed from resins which are solids or semi-solids, composed of a complex, amorphous mixture of organic substances having no definite melting point and no tendency to crystallize. Thus, cellulose and its derivatives could not be called resins, even though many of the esters of cellulose are plastics. Most resins are used in moldings, laminates and coatings. The use of resins has increased from about 2 million pounds in 1920 to about 18 billion pounds in 1970. The amounts of various plastics produced and sold in 1970 are listed in Table II. B. 10. (27:66). Polyethylene constitutes nearly a third of the plastics market while cellulosics, once the leader, comprises only about 1%. Capstain (20:25) reports that there are more than 40 different families of plastics and sometimes hundreds of individual types in each family. A brief review of the composition of some of these plastics is presented here.

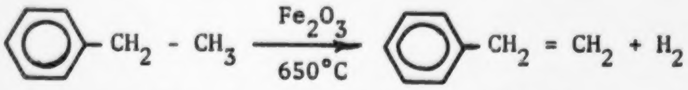
Polyethylene Polyethylene was discovered in England in the early 1930's by a group of chemists who were carrying out high pressure reactions. It is formed by the polymerization of ethylene:

$$n\,CH_2 = CH_2 \longrightarrow \{CH_2 - CH_2\}_n$$

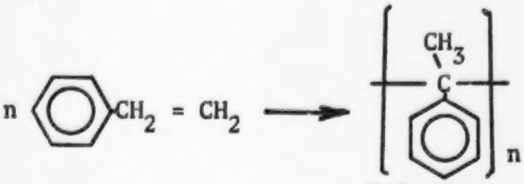
In the high pressure process (15,000 - 45,000 lb./sq. in.) ethylene reacts with itself, in the presence of a catalyst, by a free radical mechanism. When this polymer has a low degree of side chain branching, it has a tendency toward a crystalline structure, leading to a higher melting point. Its specific gravity ranges from 0.940 - 0.970, and it is called high density polyethylene. Low density polyethylene, with a specific gravity range of 0.910 - 0.935, results when side chain branches are present, producing steric hindrance which also lowers crystallinity, softening point, and viscosity.

The polyethylene plastics are non-polar resins which possess a low dielectric constant. They are used in electrical applications, as coatings on cardboard milk and juice cartons, and for containers for such liquids as milk, juice, detergent and bleach.

Polystyrene Styrene was first isolated in 1931 during the distillation of fragrant balsams from certain plants. Although coal tar was the first commercial source of styrene, today it is produced by the dehydrogenation of ethylbenzene (21:429):



Purification of styrene is difficult because of its tendency to polymerize to polystyrene:



Polystyrene

The use of styrene as a monomer began after 1930 when it was discovered that as little as 0.01% divinyl benzene would produce a brittle product through crosslinking.

Three styrene copolymers have been developed for utilization because of their properties. Acrylonitrile-Butadiene-Styrene (ABS) resins are used because they are tough, rigid and hard. They are used in sewage, drain and vent piping. Styrene-Acrylonitrile (SA) copolymers are used with a glass filler for strength. Styrene-Butadiene Rubber (SBR) is used as a synthetic rubber in automobile tires.

Polyvinyl chloride Vinyl polymers are characterized by the presence of the vinyl group $(CH_2{=}CH_2)$. When chlorine is attached, the group becomes vinyl chloride $(CH_2{=}CCl)$. Polymerization under heat and pressure with a catalyst produces a linear chain with a molecular weight between 25,000 and 150,000 times that of the hydrogen molecule:

$$n \quad CH_2 = CHCl \longrightarrow \{CH_2 - CHCl\}_n$$

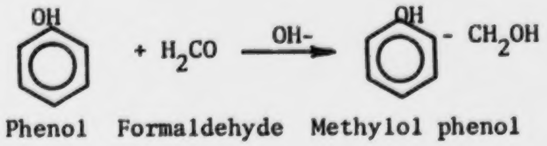
Vinyl Chloride Polyvinyl Chloride

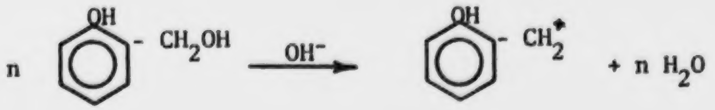
This product is thermoplastic, but long exposure to elevated temperatures results in degradation with subsequent loss of hydrogen chloride gas. It has many uses in construction, clothing, electrical, flooring, home furnishing, packaging, toys, sporting goods, auto mats and seat covers, credit and playing cards, and paint formulations.

Polyvinyl butyral is used in automobile safety glass laminates and polyvinyl acetate is used in the manufacture of adhesives.

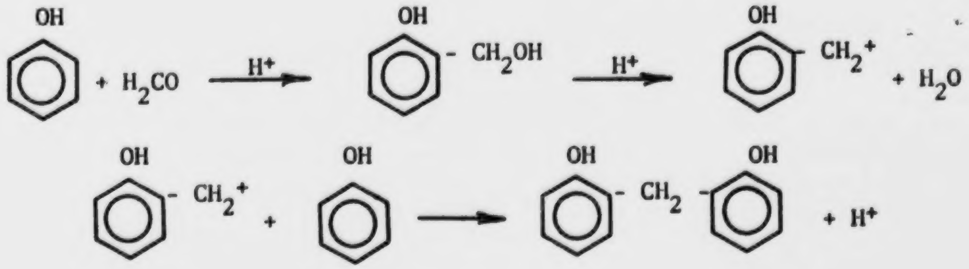
Phenolics The term "phenolic resin" includes a wide variety of products formed by the reaction of phenolic compounds with various aldehydes, such as formaldehyde or furfural. These reactions may be acid or base catalyzed.

The basic catalysts produce a one step reaction from which the resin is called "resol" type resin. The resol resins have short shelf life because they continue to react in the storage container and do not need additional curing agents:

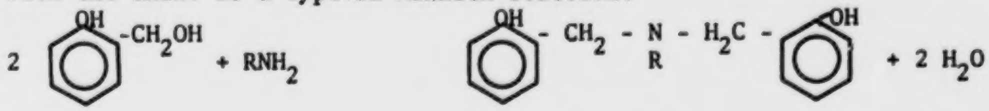

OH
+ H2CO
OH-
OH
- CH2OH
Phenol
Formaldehyde
Methylol phenol


n
OH
- CH2OH
OH-
OH
- CH2+
+ n H2O

The intermediate of the acid catalyzed reaction is also methylol phenol:

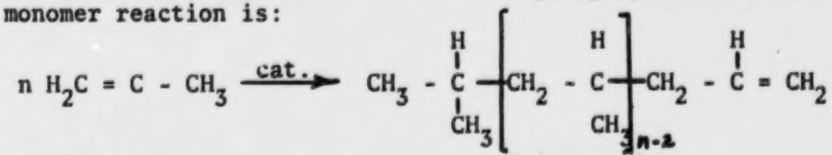

OH
+ H2CO
H+
OH
- CH2OH
H+
OH
CH2+
+ H2O
OH
- CH2+
+
OH
OH
- CH2 -
OH
+ H+

The two step, acid catalyzed reaction, produces a "novalak" resin, which requires additional crosslinking agents such as aldehydes or hexamethylene-tetramine for curing when heated. The reaction of the novalak with the amine is a typical Mannich reaction:



Phenolic plastics are widely used where heat resistance or electrical insulation is needed. Phenol-formaldehyde resins are used as binders in the plywood and particleboard industries.

Polypropylene The polypropylene homopolymer doesn't have a very high impact resistance, therefore, much of the polypropylene exists as copolymers. The monomer reaction is:

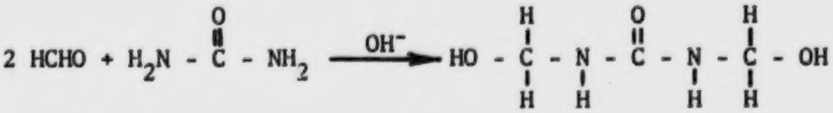


$$n\ H_2C = C - CH_3 \xrightarrow{cat.} CH_3 - \underset{CH_3}{\overset{H}{C}} \left[CH_2 - \underset{CH_3}{\overset{H}{C}} \right]_{n-2} CH_2 - \overset{H}{C} = CH_2$$

Propylene Polypropylene

In order to be useful, polypropylene must contain additives such as antioxidants and ultra-violet light absorbers. These plastics are used in filament and fibers, transportation equipment, appliances, electrical wire and cable covering, housewares, luggage and cases, packaging, toys and novelties.

Amino Resins With a suitable catalyst, urea and formaldehyde combine to form dimethylol-urea (11:1022):

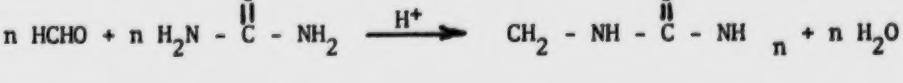


$$2\ HCHO + H_2N - \overset{O}{\overset{\|}{C}} - NH_2 \xrightarrow{OH^-} HO - \underset{H}{\overset{H}{C}} - \underset{H}{N} - \overset{O}{\overset{\|}{C}} - \underset{H}{N} - \underset{H}{\overset{H}{C}} - OH$$

Formaldehyde Urea Dimethylolurea

The methylolurea can be combined with polyhydric alcohols by a condensation process or with the acetals produced from the initial reaction of the alcohol and aldehyde.

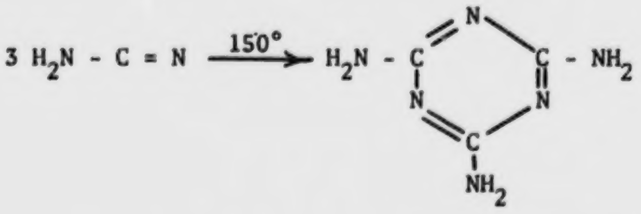
When an acid catalyst is used, urea and formaldehyde combine to form methylene urea; which polymerizes into a solid, transparent, brittle, plastic mass:



$$n\ HCHO + n\ H_2N - \overset{O}{\overset{\|}{C}} - NH_2 \xrightarrow{H^+} CH_2 - NH - \overset{O}{\overset{\|}{C}} - NH_{\ n} + n\ H_2O$$

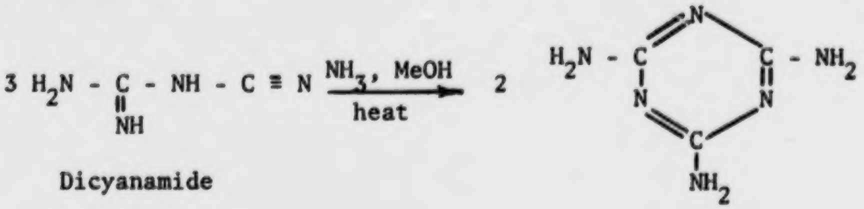
The properties of this polymer are usually modified by adding wood flour or some other suitable extender.

Malamine is produced by heating cyanamide (6:156):



Cyanamide Melamine (Cyanuramide)

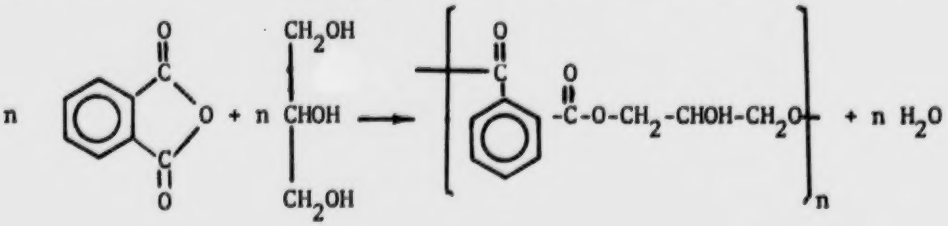
or by heating dicyandiamide in the presence of anhydrous ammonia and methyl alcohol (17:245):



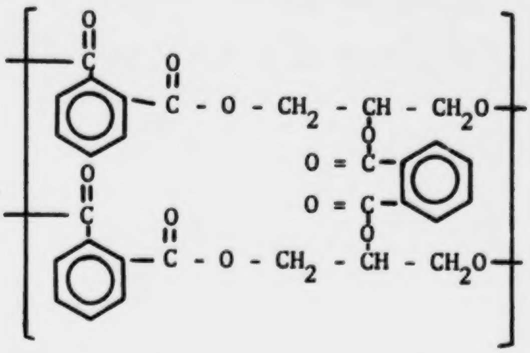
Dicyanamide

The amino group of melamine then reacts with the formaldehyde molecule to form the methylol group which takes part in the final polymerization reaction. Other amines which can be used to make amino plastics include benzoguanamine, ethyleneurea, thiourea and analine.

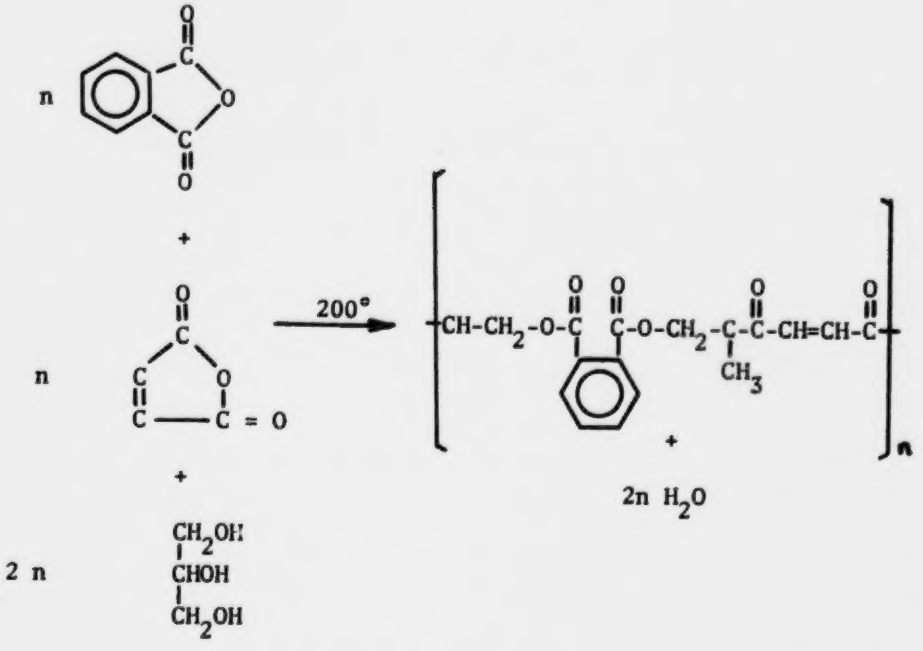
Polyesters One of the earliest polyester resins was of the glyptal type, which was made from glycerine and phthalic anhydride:



Excess phthalic anhydride serves to crosslink polymer chains:

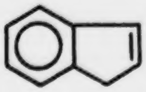


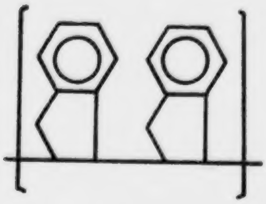
To make a resin that is compatable with styrene, an unsaturated polyester resin can be made by heating a mixture of phthalic anhydride, maleic anhydride and propylene glycol. By controlling the acidity, and using an excess of propylene glycol, the polyester formed can be cut with styrene. The rigidity of the final product is controlled by varying the ratio of aromatic anhydride to maleic anhydride, or by use of a more flexible glycol such as diethyl glycol:

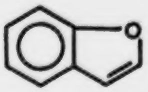


Unsaturated polyester resins have dominated the reinforced plastic market for many years because they are economical, easily fabricated, lightly colored and have excellent physical properties. They are used for body putty, buttons, cultured marble, clay pipe seal, surface coating, radomes, and boat hulls.

Coumarone Indene Resins Coumarone resins are prepared by the polymerization of a mixture of benzofuran (coumarone) and indene below 20°C using a suitable catalyst such as sulfuric acid. Although the polymerization of coumarone has not been studied extensively, as has indene, the mechanism involved is probably similar:

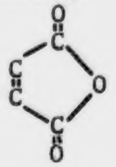

Indene


Polyindene


Coumarone

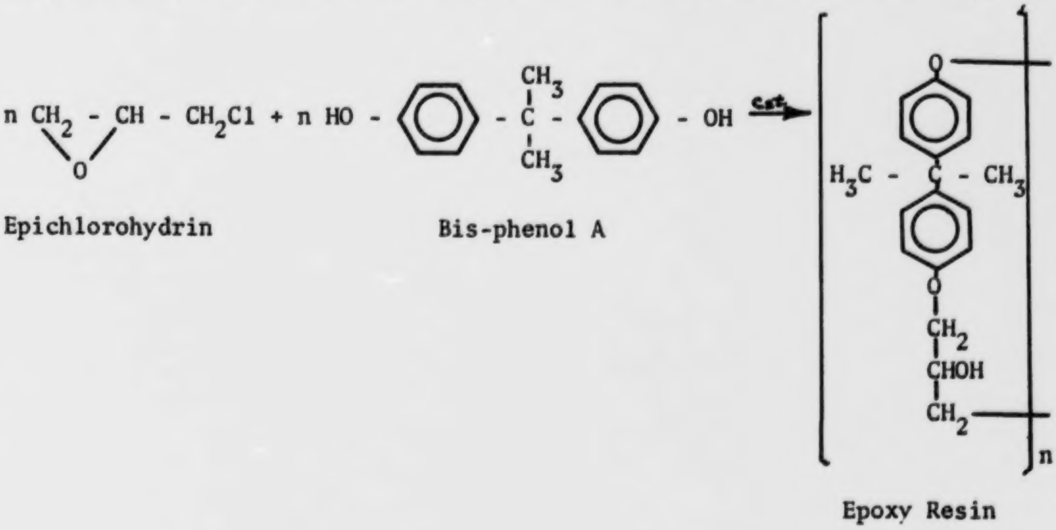
These resins are used primarily in varnishes, rubber products, linoleum, floor tiles and mastic for flooring.

Alkyd Resins Alkyd resins are formulated from polyesters. An ester is formed by the reaction of an alcohol with an acid or anhydride. By selecting a polyfunctional alcohol and a polyfunctional acid, a large number of repeating units can be formed. If the acid is unsaturated as with maleic acid or maleic anhydride,


Maleic Anhydride

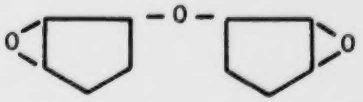
the resulting esters will be unsaturated. Polyesters are formed by the addition of an unsaturated monomer such as methacrylate, styrene, vinyltoluene, or triallylcyanurate. Although this mixture begins to react immediately upon contact, the reaction rate is extremely low at room temperature, so a catalyst is needed. The final product is a polyester that has been crosslinked at its sites of unsaturation by a method similar to that used to crosslink the polyenes.

Epoxy Epoxy resins are formed by reacting epichlorohydrin with a polyhydroxy compound such as bisphenol-A in the presence of a catalyst:



Epoxy resins are thermoplastic resins, but are easily converted to tough, infusible solids by addition of curing agents and/or an accelerator (4).

Epichlorohydrin has been reacted with other types of resins such as novalac resins, aminophenols and other polyhydric materials to produce plastic materials. One of the newer epoxy resins is made by reacting cyclic olefins with peracetic acid to produce epoxide groups attached directly to the rings:



These cycloaliphatics have superior weatherability, arc and tracking resistance, and dielectric strength.

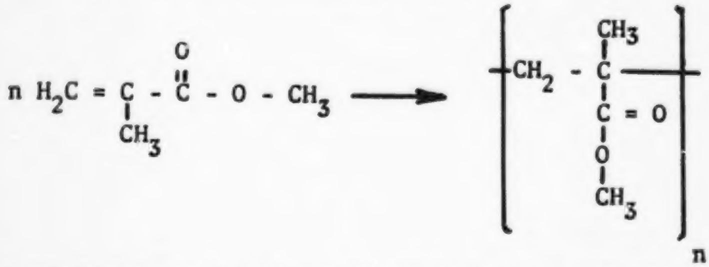
Epoxy resins are used in protective coatings, reinforced plastics, and bonding and adhesives for auto primers and plant maintenance.

Acetal Plastics The molecular structure of the acetal plastics is that of a linear acetal, made up of chains of unbranched oxymethylene groups:

$$\left[O - CH_2 - O - CH_2 - O - CH_2 \right]_n$$

The resin has high crystallinity and high melting point making it a suitable replacement for metal in some applications. Gears, foot valves, bearings, ballcocks, and showerheads have been made from acetal homo-and co-polymers.

Acrylic Plastics Acrylic resins consist of long chain, linear molecules formed by the polymerization of acrylic or methacrylic esters in the presence of a suitable catalyst:

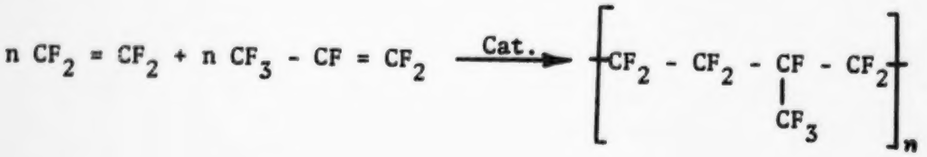


$$n\,H_2C = \underset{\displaystyle CH_3}{\underset{|}{C}} - \overset{\displaystyle O}{\overset{\|}{C}} - O - CH_3 \longrightarrow \left[CH_2 - \overset{\displaystyle CH_3}{\overset{|}{C}}\!\!\begin{array}{l} \\ | \\ C = O \\ | \\ O \\ | \\ CH_3 \end{array} \right]_n$$

These products are noted for their light transmission, clarity, and resistance to sunlight and weathering. Modified acrylics have a much higher impact strength than the general purpose acrylic.

Some of the common trade names for acrylic plastic resins are Lucite, Crystallite, Plexiglas, and Perspex. They are used for aircraft canopies, windows, instrument panels, searchlight covers, and aquariums.

Fluorocarbon Plastics The fluorocarbon plastics are analogs of the olefins with some of the hydrogens replaced by fluorine atoms. The reaction producing the polymer is similar to that used for the other olefins:

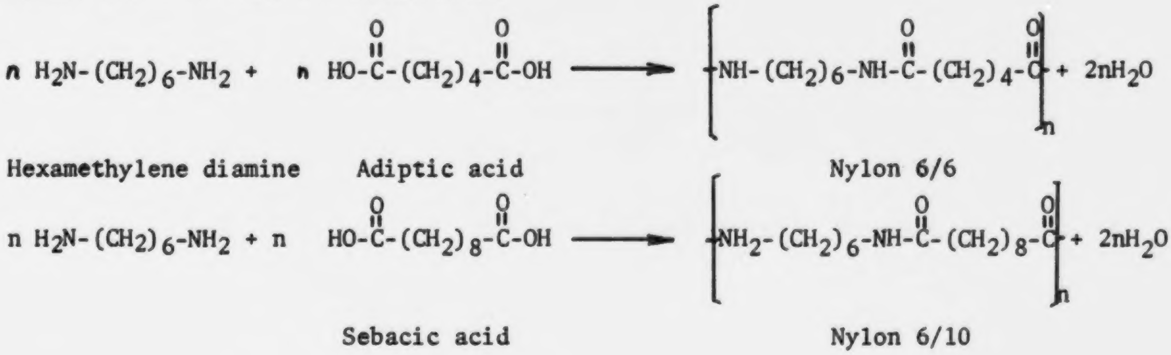


$$n\,CF_2 = CF_2 + n\,CF_3 - CF = CF_2 \xrightarrow{Cat.} \left[CF_2 - CF_2 - \underset{\displaystyle CF_3}{\underset{|}{CF}} - CF_2 \right]_n$$

These compounds exhibit chemical inertness, resistance to temperature extremes, essentially no moisture absorption, low coefficient of friction, low flammability, and weather and oxidation resistance.

Other similar plastics are the copolymer plastics and the chloro-fluoro-carbon plastics. These plastics have good electrical, thermal and chemical properties which give them a wide range of uses. One such plastic, teflon, is used as a lining on cookware for non-sticking and greaseless cooking, and in containers for highly corrosive materials.

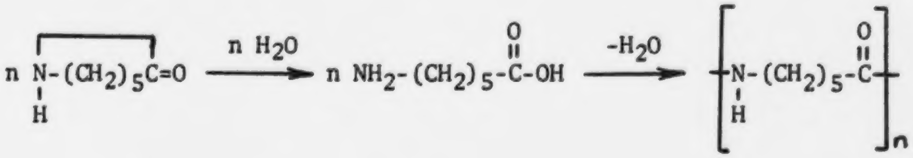
Polyamide Plastics (Nylons) Nylons are polyamides formed by condensation of dibasic amines or by polycondensation of amino acids. Nylon 6/6 is made by condensation of a 6 carbon diamine and a 6 carbon dibasic acid while nylon 6/10 is formed by condensation of a 6 carbon diamine and a 10 carbon dibasic acid:



$$n\,H_2N-(CH_2)_6-NH_2 + n\,HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH \longrightarrow \left[NH-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n + 2nH_2O$$

$$n\,H_2N-(CH_2)_6-NH_2 + n\,HO-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-OH \longrightarrow \left[NH_2-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}\right]_n + 2nH_2O$$

Nylon 6 is made by the hydrolysis of ε-caprolactam followed by condensation.

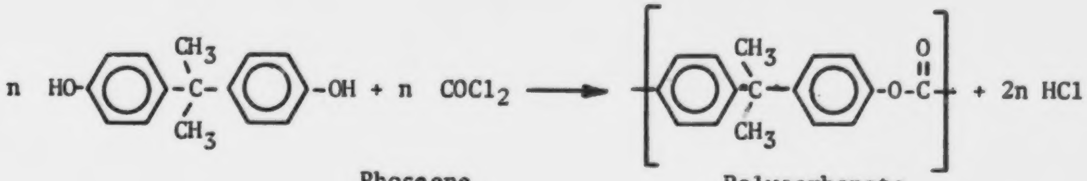


$$n\,\underset{H}{N}-(CH_2)_5C{=}O \xrightarrow{n\,H_2O} n\,NH_2-(CH_2)_5-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{-H_2O} \left[\underset{H}{N}-(CH_2)_5-\overset{O}{\overset{\|}{C}}\right]_n$$

ε-caprolactam is prepared from cyclohexanonoxime which is produced by the reaction of hydroxylamine and cyclohexanone. Benzene and phenol, the byproducts of coke plants, can be converted to cyclohexanone.

Copolymers of nylon offer a wide range of properties, while blends and grafts are used within the plastic industry because they impart toughness and desirable performance characteristics.

Polycarbonate Resins Polycarbonate plastics are prepared by ester exchange between dialkylcarbonate and dihydroxyaromatic compounds or by phosgenation of a dihydroxyaromatic compound, such as bisphenol A:

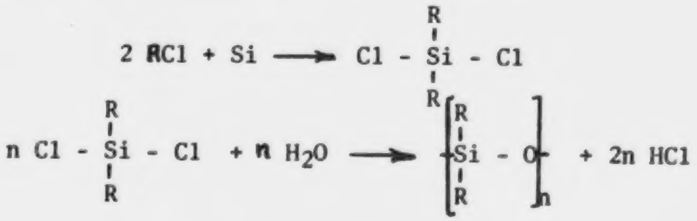


Phosgene

Polycarbonate

Polycarbonates are characterized by high impact strength, dimensional stability, heat resistance, transparency, and other desirable properties. They are used for airplane canopies and safety glass lenses where high impact strength is required.

Silicones Silicones are semi-organic polymers containing silicon, oxygen, and an organic compound. One method of preparation is to reduce quartz to silicon and react it with methylchloride. This product is then hydrolyzed to the polyorganosiloxane:



$$2\,RCl + Si \longrightarrow Cl - \overset{R}{\underset{R}{Si}} - Cl$$

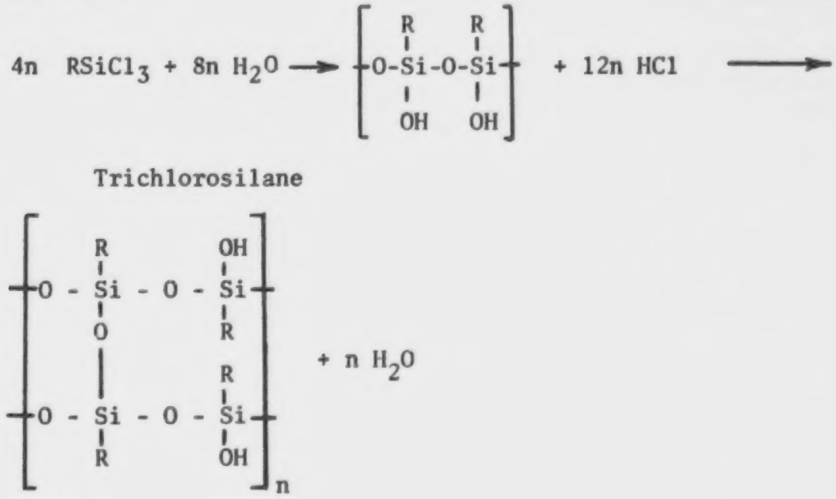
$$n\,Cl - \overset{R}{\underset{R}{Si}} - Cl + n\,H_2O \longrightarrow \left[\overset{R}{\underset{R}{Si}} - O \right]_n + 2n\,HCl$$

Dichlorosilane

Polyorganosilane

The silicones of greatest value are resistant to weathering and oxidation, repellent to water, have good electrical properties, and are incompatable with most organic polymers (can be used as mold releases).

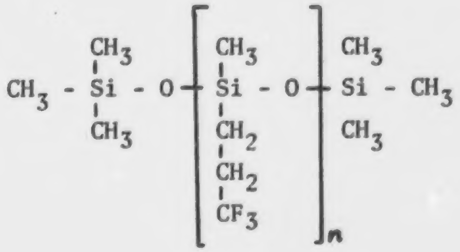
Hydrolysis of the pure dichlorosilanes can give only linear polymers which are oils or greases (21:605). If trichlorosilanes are hydrolyzed, crosslinking of the chains after hydrolysis produces three dimensional solid resins:



$$4n\ RSiCl_3 + 8n\ H_2O \rightarrow \left[-O-\overset{\overset{R}{|}}{\underset{\underset{OH}{|}}{Si}}-O-\overset{\overset{R}{|}}{\underset{\underset{OH}{|}}{Si}}- \right] + 12n\ HCl \longrightarrow$$

$$\left[\begin{array}{c} -O-\overset{\overset{R}{|}}{\underset{\underset{O}{|}}{Si}}-O-\overset{\overset{OH}{|}}{\underset{\underset{R}{|}}{Si}}- \\ \quad | \qquad\qquad\qquad \\ -O-\underset{\underset{R}{|}}{Si}-O-\overset{\overset{R}{|}}{\underset{\underset{OH}{|}}{Si}}- \end{array} \right]_n + n\ H_2O$$

It follows that by changing the proportion of dichloro and trichlorosilanes present, the properties of the silicone resin produced could be varied. Other molecules are introduced into the siloxane molecules to modify the properties of the resin. One of these molecules - fluorine - has profound effects on the solubility of the silicone compounds. These fluorinated silicones are insoluble in almost all solvents and can be shown as:

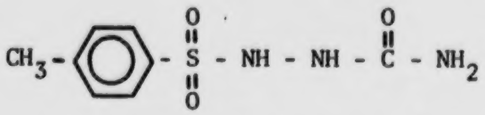


$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-O-\left[\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CF_3 \end{array} \right]_n \overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

Foam Plastics Almost any plastic can be used to form a foam plastic (5, 7, 18, 26, 32, 33). Although styrene and polyurethane foams are probably two of the most widely recognized foams today, cellulosic foams have been used in the past. Thermosetting plastics such as phenolics (32) and ureas (7) produce light weight, brittle foams which are good heat-resistant insulators.

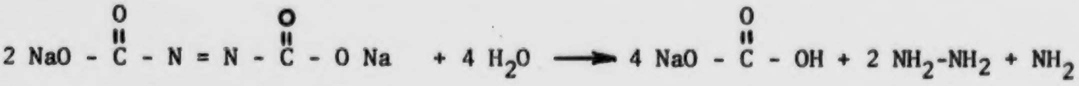
Foams may be rigid, semi-rigid, or flexible and may be formed with or without skins. The differences between the normal plastic and a foam is the density, the residue left in the cells by the blowing agent, and their uses.

Blowing agents may be low boiling solvents that evaporate rapidly to cause foaming, or they may be nitrogen containing compounds, such as azobisformamide, N-nitroso compounds, and sulfonylhydrazides, that decompose to produce nitrogen. A typical blowing agent is p-toluenesulfonyl semicarbazide:



One gram of this material produces 143-145 c.c. of gas at standard temperature and pressure (12). The composition of the gas produced is 62% nitrogen, 30% carbon dioxide, and 4% carbon monoxide (5:27), the non-gaseous products are toluene disulfide, ammonium sulfinate, and ammonium carbonate.

Another blowing agent, which reacts with water, is sodium azodicarboxylate, which decomposes to nitrogen in the following way (5:29):



$$2\ NaO - \overset{O}{\overset{\|}{C}} - N = N - \overset{O}{\overset{\|}{C}} - O\ Na \quad + 4\ H_2O \longrightarrow 4\ NaO - \overset{O}{\overset{\|}{C}} - OH + 2\ NH_2\text{-}NH_2 + NH_2$$

Sodium Azodicarboxylate

The hydrazine formed can react further if lead peroxide is employed as the curing agent, as shown by the following equation:

$$H_2N - NH_2 + 2\ PbO_2 \longrightarrow N_2 + H_2O + 2PbO$$

The lead compounds present are potential health hazards.

Additives Most plastics include some additives which impart desirable properties to the product allowing a wider range of utilization. Although most additives are present in very low concentrations, they could affect the reaction rate or products of chemical processes. A brief description of some typical additives are given below.

Plasticizers are low melting solids or low volatile liquids, very often esters which impart desirable qualities such as flexibility and ease in processing to the plastic. Plasticizer molecules mixed with the plastic weaken the van der Waals forces, usually without reacting with the polymer.

Plasticizers are chosen with regard for toxicity, odor, heat resistance and solvent resistance as well as the product flexibility, hardness, flammability and utilization. In addition, the physical and chemical properties of a particular plasticizer are important from a standpoint of color, handling, acidity, moisture content and compatibility with the resin.

Some general classes of plasticizers include phthalate esters, adipate esters, azelate esters, sebacate esters, phosphate esters, epoxy esters, biphenyls, ether derivatives, glycerol esters, glycol derivatives, petroleum derivatives (mineral oil, etc.), polyesters, styrene derivatives, sucrose derivatives, and sulfonic acid derivatives.

Ultraviolet absorbers are used to reduce polymer degradation caused by ultraviolet light, with a wavelength between 400 and 290 mμ, which has sufficient energy to break most chemical bonds in organic molecules. This type of degradation results in crazing, color change, decreased strength and loss of flexibility.

Light energy can be disposed of by the molecule in one or more of the following ways:

a. emit a photon - fluoresce and return to its original state,
b. give up its energy in the form of heat after distributing the energy over several bonds,
c. undergo a reversible photochemical change, give off heat, and return to its original state, and
d. transfer its energy to another molecule. Ultraviolet absorbers work in two ways to protect the polymers from degradation by UV light; by absorbing (screening) most of the incident light so the polymer does not acquire the excited state, and by acting as an energy transfer agent, absorbing most of the energy from the polymer molecule before it can undergo alteration, thus quenching the excited state. Most UV stabilizers are screening agents, but nickel and some of the heavy metals form complexes which act only as excited state quenches.

Absorbers are selected with regard for their color, compatibility with the plastic and plasticizer, toxicity, and resistance to water and solvents.

Typical classes of UV absorbers are benzophenones, benzotriazoles, benzylidene malonates, salicylates, substituted acrylonitriles, organic nickel, monobenzoates, and indole derivatives. They are usually used in concentrations of less than 2%.

Colorants are classified as pigments (inorganic and organic) or dyes. Pigments are finely divided solids which are dispersed in the system being colored, while dyes are materials which dissolve in the resin.

Colorants are chosen with regard for cost, hue (red, yellow, blue, etc.), value (degree of lightness and darkness), chroma (intensity of a distinct hue, degree of color departure from gray of same lightness), strength (quantity of color when mixed with titanium dioxide will give a depth of shade equal to a given weight of some other color mixed with TiO_2), and opacity (the measure of a colorants ability to stop light transmission).

Some colorants, such as the cadmium sulfides, selenides, and cadmium mercury compounds, could prove to be a problem in waste disposal systems if they became concentrated or leached into the ground water.

Antioxidants are used to combat oxidative degradation during processing, manufacture, and storage. They must be able to withstand the effects of heating during processing. In general, heat and light stabilizers are not antioxidants.

Typical antioxidants are alkylated phenols, alkylated bisphenols, alkylidene polyphenols, thio and dithio polyphenols, amines, organic phosphates, and hydroquinones.

Stabilizers are used to retard the rate of degradation caused by heat, light, oxidation, etc. In view of the knowledge of degradation the perfect stabilizer would be a compound that would screen ultraviolet light, absorb free radicals, offer oxidation protection, react with resin impurities, and protect against the disruption of double bonds, however, stabilizers should not have detrimental effects on the clarity of the product, be prone to discoloration, plate out, or be toxic.

Typical stabilizers are barium chloride powders or liquids, barium cadmium zinc powders or liquids, barium carbonate, barium lead, barium silicate complexes, calcium powders, some epoxides, nitrogen compounds, phenols, phosphates, tins and ureas.

Flame retardants, both additive and reactive types, are used to reduce the hazards to life and property caused by flammable plastics (1, 9, 10, 23, 24, 25, 28 30). Certain chemical agents are known for their ability to impart flame resistance, including the halogens (chlorine, bromine, fluorine), phosphorus, and antimony. It is a common practice to use the halogens in conjunction with phosphorous to formulate flame retardants. Boron is used to a limited extent because of technical problems related to compounds containing this element.

Obviously, some resins have inherent flame resistance, such as polyvinylchloride and the flurorcarbons, but it is necessary to use flame retardant additives with most plastics. Some typical flame retardants are the phosphate esters, chlorinated paraffins, halogenated phosphates, halogenated aromatics, ammonium bromide, antimony oxide, zinc borate, bromine containing polyyols, and tetrabromo-bisphenol A.

Fillers and extenders are used for reinforcement, reducing the required amount of resin to lower the product cost, and to add beauty or strength as with the addition of marble chips to vinyl flooring. Almost all fillers give a small amount of reinforcing action when added to polymers. While most fillers are inert, there is evidence that there may be strong attraction between some fillers and the functional groups in some resins.
The major types of fillers are:

a. Silica products such as sand, quartz, or diatomaceous earth, and pyrogenic silica products such as fumed coloidal silica,

b. Silicates including mica, kaolinite, talc, and asbestos, as well as the synthetic silicates such as calcium and aluminum silicate,
c. Glass in the form of flakes, spheres, fibers and even microballons,
d. Metal oxides such as alumina, magnesia, and titania,
e. Other inorganics such as barium sulfate, silicon carbide and molybdenum disulfide,
f. Metals such as bronze, aluminum, lead and stainless steel which are added primarily for beauty,
g. Carbon black for all types of elastomers and
h. Organic fillers such as wood flour, pulp, etc.

Fiber reinforcement is attained with cellulose fibers, synthetic fibers, dacron, orlon or nylon, carbon fibers, glass fibers, asbestos fibers, metallic fibers and ceramic fibers.

Processing aids are used to control viscosity, stabilize an emulsion, provide lubrication during processing, assist a mold release, prevent blocking and adhesion, or improve the formation of a filled molding compound.

The viscosity depressants are not the same as the plasticizers, but are used to lower the viscostiy of the plastisol without the use of additional plasticizer. Quite often the compounds will be ethoxylated fatty acids.

The parting or mold release agents can be sprayed directly on the mold or incorporated into the plastic itself. Examples are waxes, silicones, fluorocarbons, and soaps. Their purpose is to prevent the plastic from sticking to the mold.

Emulsifiers and compounds that help preserve the resin in a heterogenous system of one immiscible liquid dispersed in another. They may be anionic, cationic, or non-ionic in nature and in the case of water emulsions, they could be detergents.

Internal lubricants are somewhat like the mold release agents in that their major function is to prevent the plastic or rubber from sticking to the processing equipment. Very commonly the internal lubricants are waxes or metallic soaps.

Anti-blocking agents are designed to prevent two surfaces from permanently adhering to each other. These anti-blocking agents must have partial compatibility and yet exude from the surface under desired conditions to perform their function. Again, the blocking agents are often waxes, oils, salts of fatty acids, and even polymers.

Silane coupling agents (14) improve the coupling between the inorganic reinforcement agent and the organic polymer. This is generally carried out through a chemical reaction or series of chemical reactions. A very small amount of the right silane will give a large improvement in the product, especially in the cases where the additives are koalin clays, silicas, and silicates.

Other additives include the peroxides, for generation of free radicals to crosslink unsaturated compounds; and the anti-static compounds which may be amines, ammonium compounds or anionic compounds designed to bleed off static electric charges.

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Table II. B. 1. Composition of Typical Municipal Refuse as Reported by Kaiser (13).

Category	Weight Percent	
Paper		53.46
Corrugated paper boxes	23.38	
Newspaper	9.40	
Magazine paper	6.80	
Brown paper	5.57	
Mail	2.75	
Paper food cartons	2.06	
Tissue paper	1.98	
Wax cartons	0.26	
Plastic coated paper	0.76	
Moisture		9.05
Garbage		8.40
Vegetable food wastes	2.29	
Citrus rinds & seeds	1.53	
Meat scraps, cooked	2.29	
Fried fats	2.29	
Glass, Ceramics, Ash		7.73
Vegetation		
Ripe tree leaves	2.29	
Flower garden plants	1.53	
Lawn grass green	1.53	
Evergreen	1.53	
Metals		6.85
Miscellaneous		7.62
Wood	2.29	
Plastics	0.76	
Rags	0.76	
Leather goods	0.38	
Rubber compositoon	0.38	
Paint and oils	0.76	
Vacuum cleaner catch	0.76	
Dirt	1.53	
Total		99.99

Table II. B. 2. Composition of Municipal Wastes Collected in Various States as Reported by Hickman (8).

wt.% (wet basis)

	CALIFORNIA	NEW JERSEY	TENNESSEE	ARIZONA	ILLINOIS	OHIO	NEW YORK
Paper	54	51	46	43	42	42	40
Food	15	10	26	22	14	28	10
Metal	7	8	11	10	9	9	8
Glass	2	4	11	8	6	8	-
Wood	2	4	1	2	-	3	7
Misc.	2	4	5	1	-	3	3

Table II. B. 3. Industrial Wastes by Categories

Rubber-Plastics

- Shredded rubber
- Tires
- Foam Rubber
- Plastic wastes
- Fiberglass wastes
- Rubber Scraps

Mixed Sludges

- Treatment plant sludge
- Lagoon sludge
- Settling basin sludge

Fruit-Vegetable Wastes

- Fruit wastes
- Vegetable wastes
- Dough wastes
- Grain wastes

Glass Wastes

- Glass bottles

Paper Waste

- Corrugated
- Paper bags
- Paper drums
- Office waste
- Cafeteria waste
- Washroom waste

Wood Waste

- Bark
- Lumber
- Pallets
- Sawdust
- Sanding dust
- Wooden crates
- Wooden boxes
- Trimmings
- Skids

Sand and Stone Wastes

- Bricks
- Tailings
- Tiles
- Sand
- Concrete
- Ashes

Metal Wastes

- Banding
- Strapping
- Metal Scraps
- Buckets
- Barrels
- Cans
- Wire
- Turnings
- Burnings
- Slag

Animal Wastes

- Animal offal
- Hair
- Feathers
- Hides
- Leather scrap
- Bones
- Shells
- Paunch
- Fish
- Seafood

Petro-Chemical Wastes

- Waste Inks
- Paints
- Oils
- Solvents
- Thinner
- Resins
- Glues
- Asphalt
- Pesticides
- Herbicides

Textile Wastes

- Rags
- Upholstery scraps
- Drapery scraps
- Apparel scraps
- Canvas & burlap
- Cotton & wool
- Textile bags

Table II. B. 4. Estimate of Industrial Waste Composition in Oregon

Volume Percent

	Paper Waste	Wood Waste	Metal Waste	Animal Waste	Textile Waste	Petro- Chemcl	Fruit Vegtbl	Rubber Plastic	Sand, stn Glass, Ash
Meat Processing	97	3	>1						
Electric Machinery	97	1						1	
Dairy Products	96	>1						3	1
Misc. Food Processes	94	1					3		>1
Printing & Publication	94	4	1			>1			
Petroleum & Allied	92	5							3
Scientific Instrument	88	5	1		>1	>1		5	
Ordnance	85	11	1			2			
Non-Elec. Machinery	82	13	3					2	
Processed Foods	70	>1	5				23	2	
Apparel Products	69	1	1		28			1	
Rubber & Plastics	69	13	1		1	>1		16	
Chemical & Allied	60	27	8			8			1
Transportation	58	40	1		1				<1
Misc. Manufacturing	57							43	
Cannery & Frozen	56	3	2			>1	39	>1	
Textile Mills	54	2	1		42	>1		>1	<1
Furniture	52	39	4		3			1	<1
Stone, Clay & Glass	44	40	5			>1		>1	11
Seafood Processing	43	13	10	33				1	
Fabricated Metals	43	43	14						
Primary Metals	30	7	15			>1			47
Wood Products	27	65	6			1		1	<1
Paper & Allied	25	4	1						<1
Leather Manufacture	14	2	4	72	>3			3	2

Table II. B. 5. Composition of Poultry Manures

wt.% (air dry basis)

	Hen Manure	Broiler Manure
Moisture	4.29	
Ash	23.28	20.83
Crude Fiber	12.15	
Ether Extract	1.38	
Crude Protein	19.94	32.21
True Protein	10.13	11.42
Calcium	6.50	5.50

Table II. B. 6. Composition of Manures of Different Animals

wt.%

	Water	Nitrogen	Phosphorus	Potassium
Chicken	54	1.56	0.40	0.35
Dairy cattle	79	0.56	0.10	0.50
Fattening cattle	80	0.70	0.20	0.45
Hog	75	0.50	0.14	0.38
Horse	60	0.69	0.10	0.60
Sheep	65	1.40	0.21	1.00

Table II. B. 7. Composition of Cereal Straws

wt.%, dry basis

Component	Oat min. - max.	Rice min. - max.	Wheat min. - max.
Dry matter	83.9 - 95.2	88.8 - 93.4	82.8 - 99.1
Cellulose	40.1		35.3 - 63.9
Lignin	13.4 - 15.8		12.4 - 15.1
Pentosans		17.7	10.2 - 12.8
Crude protein	2.0 - 8.6	2.8 - 6.2	1.5 - 6.9
Crude fat	0.8 - 3.2	8.7 - 2.3	1.0 - 3.7
Crude fiber	33.3 - 54.0	27.6 - 38.3	36.4 - 51.5
Ash	4.9 - 12.9	14.0 - 20.1	3.5 - 11.1
Sulfur	0.20 - 0.27		0.13 - 0.29
Sodium	0.23 - 0.53	0.31	0.06 - 0.23
Chlorine	0.70 - 0.85		0.21 - 0.34
Calcium	0.13 - 0.40	0.15 - 0.38	0.10 - 0.42
Phosphorus	0.15 - 0.43	0.06 - 0.15	0.04 - 0.51
Potassium	0.20 - 2.41	1.10 - 1.51	0.12 - 1.95
Magnesium	0.16 - 1.48	0.07 - 0.18	0.05 - 0.70
Iron	0.018- 0.056		0.007- 0.017

Table II. B. 8. Composition of Grass Seed Straws

wt.%, dry basis

Component	Fine Chewings Fescue	Merion Bluegrass	Highland Bentgrass	Perennial Ryegrass	Annual Ryegrass
Crude protein	5.2	9.1	4.6	5.5	4.5
Crude fiber	45.1	36.6	39.4	41.2	40.2
Crude fat	1.8	2.1	1.9	1.8	1.4
Crude pectin	1.1	1.6	1.7	2.3	1.8
Ash	7.0	5.4	2.7	6.7	6.6
Total sugars	0.20	2.49	2.01	0.68	4.05
Reducing sugars	0.17	1.74	0.96	0.43	3.25
Pentosans	27.1	24.0	24.8	22.0	23.7
Lignin	10.2	8.7	9.0	8.8	8.6
Cellulose	45.2	41.6	44.2	42.3	42.8

Table II. B. 9. Composition of Some Typical Glasses.

Wt%

TYPE		CONTENT									
		S_1O_2	B_2O_2	Al_2O_2	PbO	CaO	Na_2O	K_2O	MgO	BaO	Ma_2O_3
Soft Soda	1	70.5		1.8		6.7	16.7	0.8	3.4		
	2	69		4		5.8	17.5	1.9	1.6		
	3	69.3		3.1		5.6	16.8	0.6	3.4		
	4	73.6	1.2			5.37	17.23		3.67		
Lead	5	56.5		1.5	29	0.2	5.6	6.6	0.6		
	6	57		1.5	29.4	0.2	4.1	7.3	0.4		
	7	63.1		0.28	20.22	0.94	7.6	5.54			0.88
Borosilicate	8	71	13.7	7.4		0.3	5.3	2.4			
	9	80.5	12.9	2.2			3.8	0.4			
	10	73	16.5		6		4.5				
Special	11	22.6	37	23.7		10	6.5	0.2			
Extra Hard	12	54.5	7.4	21.1		13.5				3.5	
	13	58.7	3	22.4		5.9	1.1	0.2	8.4		

Table II. B. 10. Production and Sales of Plastics in 1970

Plastic	Production	Sales
Polyethylene, low density	4300	4180
Polystyrene & copolymers	3350	3323
Polyvinylchloride & copolymers	3150	3050
Polyethylene, high density	1700	1625
Phenolics	1075	888
Polypropylene	1010	985
Urea and Melamine	710	638
All other vinyls	650	600
Polyesters	645	613
Alkyds	604	300
Coumarone-indene	340	350
Cellulosics	180	175
Epoxy	165	155
Miscellaneous	1722	1618
Total	19600	18500

Chemical Nature of the Constituents

Cellulose. Cellulose is a polysaccharide which yields only glucose upon hydrolysis. There is general agreement among workers in the field that cellulose is composed predominately of β 1,4 linked D-glycopyranose units, Figure II. C. 1.

The reactions of cellulose resemble those of the simple sugars. Since, however, all but one of the potential reducing groups of the glucose residue (the one terminating unit of the open chain) are involved in glycosidic linkages between individual members of the chain, cellulose lacks the pronounced reducing power of most of the sugars. The chief reactions of cellulose are those of its hydroxyl groups.

All glucose residues except one (the other terminating unit) possess three free hydroxyl groups, the one in the C-6 position being of primary nature and those in the C-2 position and the C-3 position being of secondary nature. These free hydroxyl groups react as alcohols to form addition compounds with alkalies and certain complex salts. Under certain conditions they also react with sodium metal to form compounds (comparable to the alcoholates) called cellulosates. Furthermore, the hydroxyl groups of cellulose react to form esters and ethers, and on oxidation are converted stepwise into carbonyl and carboxylic groups.

The reaction product of cellulose and sodium hydroxide, called alkali cellulose, is used in the production of cellulose xanthate and cellulose ethers. A variety of cellulose ethers can be prepared by reacting alkali cellulose with various alkyl chlorides. Similarly a variety of cellulose esters can be prepared by reacting cellulose with various organic acid anhydrides.

Acid hydrolysis of cellulose produces glucose which can be converted to hexane by reduction with hydrogen iodide and red phosphorus or to sorbitol by reduction with sodium amalgam.

Cellulose can be degraded both thermally and chemically. The main products of thermal decomposition are carbon, carbon dioxide, and water. Some of the other products formed are acetic acid, acetone, formic acid, formaldehyde, furfural, hydroxymethylfurfural, ethene, carbon monoxide, and methane. A summary of the quantity of products produced by the thermal decomposition of cellulose (9) are listed in Table II. C. 1.

The end product of the hydrolysis of cellulose is glucose, but continued chemical action on the glucose results in the formation of hydroxymethylfurfura which produces levulinic acid and formic acid. Oxalic acid can be produced from cellulose by alkaline oxidation (5) or nitric acid oxidation (15). Under some conditions the alkaline degradation of cellulose can result in complex fragmentation reactions producing formic, acetic, glycolic, and lactic acids (16).

Cellulose derivatives are used for a variety of purposes. Some of the uses of cellulose derivatives are listed in Table II. C. 2.

Plastics. Most plastics are generally chemically inert, however, each is affected to some degree by certain organic solvents, acids, and bases. In addition, all plastics degrade at elevated temperatures.

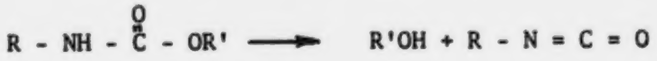
The solubility of some plastics in organic solvents is listed in Table II. C. 3. The plastics which appear to be most resistant to attack by solvents are the nylons, urethanes, polyethylene, fluorocarbons, and chlorinated polyethers.

The effect of acids and bases on certain plastics is listed in Table II. C. 4.

As with wood, paper, or other combustible materials, at elevated temperatures, plastics degrade to form combustible gases, non-combustible gases, and a char. If an oxidizing agent is present, the combustible gases will burn when heated above their ignition point. However, in the case of halogenated or flame retardant treated plastics the combustibility of the plastic is nil unless the temperature is raised much higher than the normal combustion temperature. The halogenated plastics produce acid gases such as hydrogen chloride.

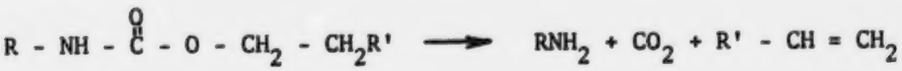
The urethane plastics show a great variation in properties. Urethane foam from tertiary alcohols may decompose at a temperature as low as 50°C, while urethanes of many primary alcohols change only slowly at 150°C. According to Saunders (2:127) there are essentially three types of reactions that can take place during the thermal decomposition of urethane:

1) a dissociation to alcohol and isocyanate,



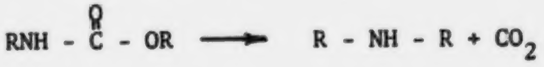
$$R - NH - \overset{O}{\overset{\|}{C}} - OR' \longrightarrow R'OH + R - N = C = O$$

2) formation of a primary amine and an olefin, and



$$R - NH - \overset{O}{\overset{\|}{C}} - O - CH_2 - CH_2R' \longrightarrow RNH_2 + CO_2 + R' - CH = CH_2$$

3) secondary amine formation.

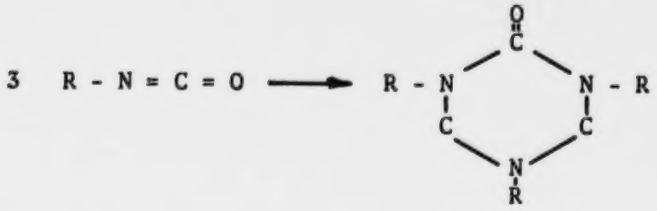


$$RNH - \overset{O}{\overset{\|}{C}} - OR \longrightarrow R - NH - R + CO_2$$

The two reactions likely to occur with isocyanates at elevated temperature are the formation of the carbodiimide and trimerization to an isocyanate.

$$2\,R-N=C=O \longrightarrow RN=C=NR + CO_2$$

Carbodiimide



Isocyanurate

When polyethylene is pyrolyzed (4) at 300 and 500°C in oxygen and wet or dry carbon dioxide, the products contain carbon dioxide, carbon monoxide, hydrogen, saturated and unsaturated aliphatic hydrocarbons, benzene, toluene, and polycyclic aromatic compounds.

The pyrolysis (not combustion) of polyvinyl chloride (8) produces hydrogen chloride, saturated and unsaturated aliphatic hydrocarbons, methyl and ethyl chlorides, and aromatic compounds.

Other studies of the products of plastic degradation have been conducted by Cerceo (3), Way and Hilado (14), Pruitt (12), Pape, et al. (10), Parish and Pruitt (11), and others (1, 6, 7).

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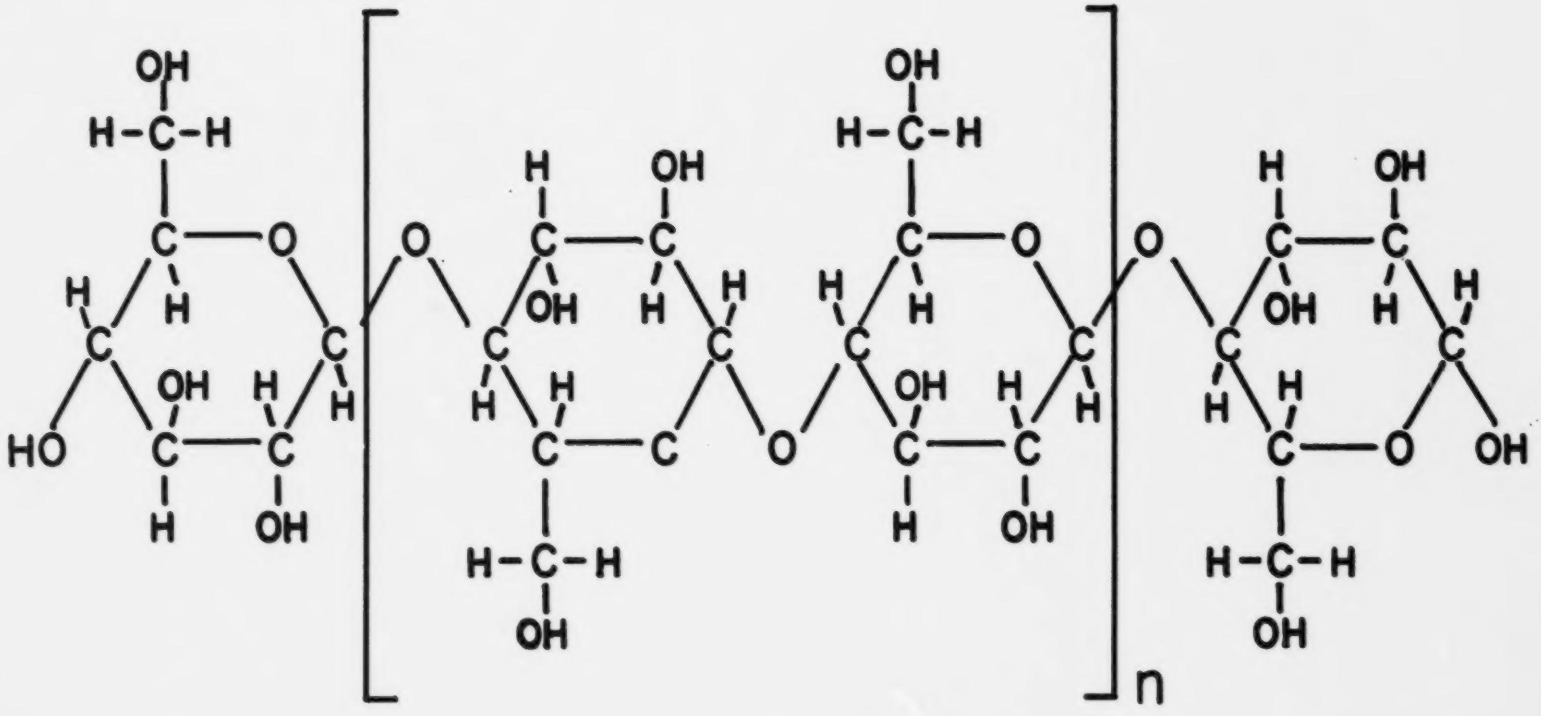


Figure II. C. 1. Schematic Diagram of a Cellulose Molecule.

Table II. C. 1. Products of Thermal Decomposition of Cellulose

	Cotton	Pine Pulp	Spruce Pulp	Birch Pulp
carbon	38.8	36.9	34.9	33.4
carbon dioxide	10.4	12.8	11.9	11.1
ethene	0.2	0.2	0.2	0.4
carbon monoxide	4.2	3.4	3.9	3.5
methane	0.3	0.3	0.2	0.5
methanol	0.0	0.0	0.1	0.0
acetone	0.1	0.1	0.1	0.2
acetic acid	1.4	2.2	2.8	3.9
other organic comp.	5.1	4.2	8.5	7.7
tar	4.2	4.8	6.3	9.6
water	34.5	34.2	30.0	29.4

Table II. C. 2. Cellulose Derivatives and Their Uses

Compound	Uses
ethyl cellulose	plastics, lacquers, sheeting, varnishes, adhesives.
methyl cellulose	adhesives, latexes, emulsions, foods, sheeting, cosmetics, pharmaceuticals.
sodium carboxymethyl cellulose	colloid, thickener.
benzyl cellulose	coatings, plastics, lacquers.
ethyl hydroxyethyl cellulose	emulsifier, thickener, stabilizer.
cellulose nitrate	lacquer, plastic, explosives.
sodium cellulose sulphate	gelatin films, glues, paints, textiles, sizing, paper, coating.
cellulose acetate	yarn, photographic films, sheeting, plastics, coatings membrane.
cellulose xanthate	fiber, cellophane, plastics, sponges.

Table II. C. 3. Solubility of Some Plastics in Selected Solvents.

	Nitrocellulose	Ethyl Cellulose	Cellulose Acetate	Cellulose Acetate-Butyrate	Vinyl Chloride Acetate	Vinyl Acetate	Vinyl Butyral	Methyl Methacrylate	Epoxy	Polystyrene	Oil Soluble Phenolic	Coumarone-Indene	Resin Modified Alkyd	Chlorinated Rubber	Modified Acrylates	Ethylene Vinyl Acetate Copolymer	Chlorinated Polyether	Fluorocarbon	Polyethylene	ABS	Polycarbonate	Phenoxy	Urethane	Nylon
Methanol	x					x	x																	
Ethanol		x					x																	
i-Propanol							x																	
n-Propanol		x					x										Resistant to most	Resistant to most	Tetrahydronaphthalene above 80°C				Resistant to most	Resistant to most - try 90% formic acid
sec-Butanol		x					x																	
n-Butanol		x					x																	
Methyl-isocutyl carbinol		x					x																	
Ethylene glycol Monoethyl Ether	x	x							x															
Ethylene glycol Monobutyl ether	x	x							x		x		x	x										
Acetone	x	x	x	x	x	x		x			x	x												
Ethylene glycol monoethyl Ether Acetate	x	x			x	x		x	x	x		x	x											
Methyl Ethyl Ketone	x	x		x	x	x		x	x	x	x	x	x							x				
Ethyl Acetate	x	x		x	x	x		x		x		x	x		x					x				
iso-Propyl Acetate	x	x				x		x		x	x	x	x		x					x				
sec-Butyl Acetate	x	x			x	x		x		x	x	x	x		x					x				
n-Propyl Acetate	x	x			x	x		x		x	x	x	x		x					x				
Methyl-i-Butyl Ketone	x	x			x	x		x		x	x	x	x							x				
n-Butyl Acetate	x	x			x	x		x		x	x	x	x							x				
n-Amyl Acetate	x	x			x	x		x		x	x	x	x							x				
Ethyl Ether	x	x			x	x						x												
Methyl Amyl Acetate	x									x	x	x	x											
Hexyl Acetate	x			x		x				x	x	x	x	x										
Isophorone	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x					x				
Benzene		x				x		x		x		x	x	x							x	x		
n-Heptane																					x	x		
Toluene		x								x		x	x	x							x	x		
Xylene		x				x		x		x		x	x	x		x				x	x	x		
Chlorinated Hydrocarbons										x														

Table II. C. 4. Effect of Acids and Bases on Certain Plastics.

Plastics	weak acids	strong acids	Effect of oxidizing acids	weak alkalies	strong alkalies
Polypropylene	resistant		attacked	none	resistant
Polystyrene	none		attacked	none	none
Polycarbonate	none	attacked		limited resistance	attacked
Pherroxy	none	resistant		resistant	resistant
Vinyl Butyral	slight	slight		slight	slight
Polyvinyl dichloride	none	none		none	none
Urethane Elastomers	dissolves	dissolves		dissolves	dissolves
Acetal	resistant	attacked		resistant	resistant
Acrylic	slight		attacked	slight	slight
Ethyl Cellulose	slight	decomposes		none	slight
Cellulose Acetate	slight	decomposes		slight	decomposes
Chlorinated Polyether	none		attacked	none	none
Fluorocarbons	none	none		none	none
Nylons	resistant	attacked		none	none
Polyethylene	resistant		attacked	resistant	resistant
Diallyl Phthalate	none	slight		none	slight
Furan	none		attacked	none	slight
Melamine Formaldehyde	none	decomposes		none	attacked
Phenol-Formaldehyde	slight		decomposed	slight	decomposes
Polyacrylic ester	swells	swells		swells	swells
Polyesters	slight	attacked		attacked	attacked
Silicons	none	slight		none	slight
Urea-formaldehyde	slight	decomposed		slight	decomposed
Epoxy Cast Resins	none	attacked		none	slight
Allyl Resin	none		attacked	none	none
Phenolis	none	slight	decomposed	slight	decomposes

CHEMICAL PROCESSES

As indicated earlier, cellulose is the single component that appears in the greatest amounts in most solid wastes. The reactions reported herein are primarily reactions involving cellulose because reclaiming and reuse of this cellulose would remove about half of the solid waste disposed of annually.

Of the many reactions possible with cellulose the primary groupings studied are crosslinking, nitrogen and phosphorus enrichment, esterification, hydrogenation, etherification, oxidation, and pulping.

The process which shows the greatest potential and will be persued to finish first is crosslinking. Crosslinking can help solve two problems at once: The disposal-reutilization of solid waste, and shortage of satisfactory building materials.

Hydrogenation is probably not economically feasible at present, however, with the rapidly dwindling petroleum supplies this may soon become not only economical, but essential.

Nitrogen and phosphorus enrichment would allow the waste to be returned to the soil as a combination soil conditioner and fertilizer. Composting alone, does not give a product that has appeal to the market because of the lack of plant growth stimulants.

Esterification and etherification lead primarily to plastics. Cellulose plastics are at present being replaced by the petro-chemical plastics, and therefore are a waning market. One new field that may require more cellulose is reverse osmosis, used in purifying water.

The products of partial oxidation may have great potential, but the time required to produce dialdehyde cellulose is so great that the economics of this process appear unsatisfactory.

Pulping may be developing again. Our dwindling forests, new pulping methods, and new straw storage methods may overcome the economic barriers that have blocked the use of straw for pulping. Reclaiming paper and adding straw pulp could greatly reduce the demands on our forests and alleviate air pollution at the same time.

Crosslinking

Since cellulose is a polymer containing chemically active hydroxyl groups, crosslinking between chains should be one means of producing a solid material. The crosslinking agents would have to be polyfunctional compounds capable of uniting with the cellulose hydroxyls of more than one cellulose chain. The fabric industry has evaluated the use of polycarboxylic acids, such as succinic acid, oxalic acid, and citric acid, to crosslink cotton cloth for improvement of its properties (4). Crosslinking may also be possible with an alkyl dihalide, resulting in ether linkages, but no known experimentation has been attempted. A third possibility for crosslinking involves use of isocyanates, which react with hydroxyls to produce carbamate esters. This reaction is the basis for rigid and soft polyurethane foam using liquid polyols. The reaction of cellulose with isocyanates has been studied by Schneebeli (14), Ellzey (6), and Hobart (11).

A variety of cellulosic wastes can be used to make a solid board using isocyanate resins including wood, straw, and paper, and although each of these wastes has been used in the laboratory to prepare small samples, extensive testing has been accomplished only with straw particleboards. Therefore this report will primarily show results achieved with straw.

Chemistry: An isocyanate compound contains the functional group -N=C=O (-NCO), while diisocyanates contain two functional groups per molecule and polyisocyanates contain many functional groups on a long chain resin. In order to achieve crosslinking between two cellulose molecules, at least two functional groups per molecule are required.

Isocyanates react with compounds which contain an active hydrogen such as alcohols, phenols, amines, amides, ureas, acids, and water. These reactions ordinarily take place without catalysts or high temperatures (3), but catalysts may be required when steric hindrance is a factor.

A brief review of isocyanate chemistry is presented here. More detailed information about the synthesis and use of isocyanates is reported by Saunders and Slocombe (13).

Aromatic isocyanates are usually more reactive than aliphatic isocyanates (3), and electronegative groups on the aromatic ring enhances reactivity, while electropositive groups reduce the reactivity.

Reactions with Hydroxyls

Water will react with isocyanates (I) as shown in Reaction 1: (R=alkyl or aryl group)

$$\underset{I}{RNCO} + H_2O \rightarrow \underset{II}{RNHCOOH} \rightarrow \underset{III}{RNH_2} + CO_2 \qquad [1]$$

$$\underset{III}{RNH_2} + \underset{I}{RNCO} \rightarrow \underset{IV}{RNH\text{-}CO\text{-}HNR} \qquad [2]$$

The carbamic acid (II) that is formed decomposes readily to produce an amine (III) and carbon dioxide. If a base is present, this reaction will proceed no further; however, in the absence of a base, the amine (III) will react with the isocyanate (I) to form a substituted urea (IV) as shown in reaction 2.

The rate of reaction of isocyanates with water depends on the particular isocyanate involved, for example octadecyl isocyanate can be emulsified and will be stable for as much as a day while others react much more readily.

Alcohols will react with isocyanates (I) as shown in reaction 3:

$$\underset{\text{I}}{\text{R-NCO}} + \underset{\text{V}}{\text{R'OH}} \rightarrow \underset{\text{VI}}{\text{R NHC O OR'}} \qquad [3]$$

The carbamate ester (VI) which is formed is sometimes called a urethane. The reaction of primary alcohols is fairly rapid but tertiary butyl alcohols react slowly, probably due to steric hindrance, and must be catalyzed. Phenolic compounds react as aromatic alcohols, but their reaction rates with isocyanates are extremely slow and must be catalyzed.

Halogen acids (VII) react with isocyanates as shown in reaction 4: (x is a halogen)

$$\underset{\text{I}}{\text{RNCO}} + \underset{\text{VII}}{\text{HX}} \rightleftarrows \underset{\text{VIII}}{\text{RNH-COX}} \qquad [4]$$

This reversible reaction produces a monosubstituted carbamyl halide (VIII), which is stable at room temperature but not at elevated temperatures. The reaction between isocyanates (I) and organic acids (IX) is shown in reaction 5:

$$\underset{\text{I}}{\text{RNCO}} + \underset{\text{IX}}{\text{R'COOH}} \rightarrow \underset{\text{X}}{\text{RNHCOOCOR'}} \qquad [5]$$

The anhydride (X) which is formed decomposes to form an amide (XI) and carbon dioxide as shown in reaction 6:

$$\underset{\text{X}}{\text{RNHCOOCOR'}} \rightarrow \underset{\text{XI}}{\text{RNHCOR'}} + CO_2 \qquad [6]$$

Cellulose should react with isocyanates because of the three hydroxyl groups on each anhydroglucose unit, however Bayer (2) speculated that cellulose would not react with isocyanates because of the "water of crystallization" left in carefully dried cellulose. He theorized that only substituted ureas would be present in the reaction mixture.

More recently, however, Hearon, et. al. (8,9), studied the reaction of aliphatic and aromatic isocyanates with dried cellulose and cellulose acetate, and found that the acetate groups could be removed by hydrolysis, and the resulting cellulose carbamate was soluble in organic solvents.

In addition, the isocyanate-cellulose reaction has been studied by Hearon and Lobsitz (10), Schneebeli (14), Eckert (5), Ellzey (7), Hobart (11), and Volozhin (15). Hearon and Lobsitz studied the aryl carbamates of cellulose including chlorophenyl carbamate and reported that the completely carbamylated product is soluble in a variety of organic solvents, but not in methanol or ethanol. Schneebeli studied the reaction of phenyl isocyanate, in anhydrous pyridine, with cellulose which had been dried at 105°C. Using x-ray study, nitrogen determination, and water sorption, he determined that the carbamate esters are actually formed and concluded that the isocyanate reacts first with the available hydroxyl units, then penetrates into the crystalline structure of cellulose to react with other hydroxyl units.

Reactions with Hydrogen attached To Nitrogen Isocyanates react with hydrogen atoms attached to nitrogen in such compounds as amines, amides, ureas, and carbamates, but the reaction rates are affected by nuclear substituents and steric hindrance.

Amines (XII) will react with isocyanates as shown in reaction 7:

$$R\ NCO + R'NH_2 \rightarrow R\ NHCONHR' \qquad [7]$$

I XII XIII

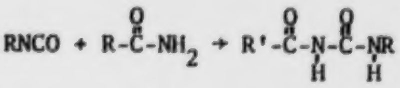
The product is a substituted urea (XIII).

Aliphatic amines are generally more reactive than aromatic amines which are more reactive than pyrrole, but these reaction rates are especially affected by steric hindrance caused by ortho-substitution of the phenyl ring. The reaction of isocyanates which contain N-H bonds is governed primarily by how basic or nucleophilic the N-H bond is; isocyanate reactivity decreases approximately in the order (1)

$$4(-NO_2) > 3(-NO_2) > 3(-OCH_3) > H > 4(-CH_3) > 4(-OCH_3)$$

whereas amine activity tends to increase in the same order.

Amides (XV) will react with isocyanates as shown in reaction 8:



$$RNCO + R-\overset{O}{\overset{\|}{C}}-NH_2 \rightarrow R'-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}R \qquad [8]$$

I XV XVI

The reaction product is a substituted biuret (XVI).

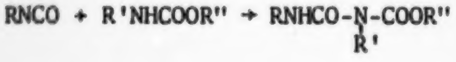
Urea (XVII) being a diamide will react with isocyanates as shown in reaction 9:

$$\mathrm{RNCO} + \mathrm{H_2NCONH_2} \rightarrow \mathrm{RNHCO\ NHCONH_2} \qquad [9]$$

I XVII XVIII

Again, the reaction product is a substituted biuret (XVIII).

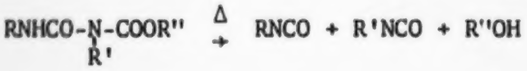
Carbamates (XIX) will react with isocyanates as shown in reaction 10:



$$\mathrm{RNCO} + \mathrm{R'NHCOOR''} \rightarrow \mathrm{RNHCO{-}\underset{\displaystyle R'}{N}{-}COOR''} \qquad [10]$$

I XIX XX

The reaction product is an allophanate (XX) which decomposes at elevated temperatures to produce two isocyanates (XXI, XXII) and an alcohol (XXIII) as shown in reaction 11:



$$\mathrm{RNHCO{-}\underset{\displaystyle R'}{N}{-}COOR''} \xrightarrow{\Delta} \mathrm{RNCO} + \mathrm{R'NCO} + \mathrm{R''OH} \qquad [11]$$

XX XXI XXII XXIII

This reaction is reversible, however, and upon cooling the allophanate may again be formed.

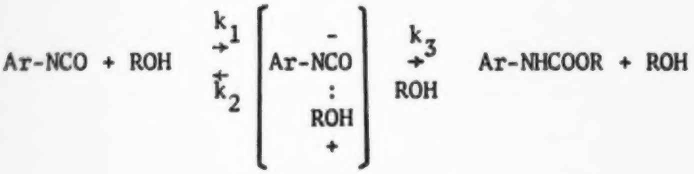
Kinetics and Mechanisms of Isocyanate Reaction

The electronic structure of isocyanates is approximated in reaction 12, with the possible resonant structures shown as:

$$\mathrm{R{-}{-}N{=}C{=}O{:}} \leftrightarrow \mathrm{R{-}\overset{+}{N}{-}C{=}O{:}} \leftrightarrow \mathrm{R{-}N{=}C{-}\overset{+}{O}{:}} \qquad [12]$$

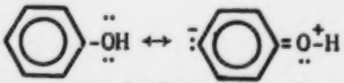
Isocyanate reactivity is affected by the composition of the aryl or alkyl group, R.

The hydroxyl groups of alcohol may catalyze the reaction between alcohols and isocyanates according to Arnold et. al. (1), reaction 13. (Ar=aryl)



$$\mathrm{Ar{-}NCO} + \mathrm{ROH} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \left[\begin{array}{c} - \\ \mathrm{Ar{-}NCO} \\ : \\ \mathrm{ROH} \\ + \end{array}\right] \underset{\mathrm{ROH}}{\overset{k_3}{\rightarrow}} \mathrm{Ar{-}NHCOOR} + \mathrm{ROH} \qquad [13]$$

It is clearly seen that alcohol with its slightly basic oxygen can act as its own basic catalyst, while phenols, being more acidic or less basic, do not catalyze themselves as well, and therefore, need the aid of a basic catalyst in order to have reasonably fast reaction times. In addition, phenols have the resonance form shown in reaction 14, which tends to lessen their basicity even more. The result is a reaction rate about equal to the very sterically hindered t-butyl alcohol.



[14]

The hydrogen attached to the nitrogen of amines will react with isocyanates to form a substituted urea. In fact, methyl isocyanate reacts nearly 200 times faster with an amine group than it does with hydroxyl groups. In a mixture of alcohol and water, the amine formed would tend to catalyze the reaction of the isocyanate with both the hydroxyl groups of water and of the alcohol, but the amine would also react with the isocyanate to form a substituted urea.

Process: A schematic diagram of the process is shown in Figure III. B. 1 Baled straw is milled to reduce the particle size, and is dried to reduce the water content. The fines are removed by screening and the isocyanate resin is applied by air spraying. The mixture is pressed into a solid board with a heated-platen hydraulic press. The boards are then finished and stored. If the straw contains 15% moisture, and 5% resin is applied, 120 pounds of baled straw will be needed to produce 100 pounds of finished board with 5 pounds of trim. Theoretically the trim could be passed through the process again but no allowances were made in the diagram for this operation.

A discussion of some of the variables involved in each step of the process is given below.

Straw Type Theroetically, any straw could be used in this process to form a straw particleboard, but differences in composition and structure may affect both the physical properties and appearance of the board. The only differences in physical properties that have been measured thus far show that the physical properties of cascade fescue and hard fescue are significantly lower than the physical properties of annual ryegrass when the three straws are processed in the same way (Figure III. B. 2.). Differences in appearance are also noticeable between such straws as annual ryegrass, cascade fescue, hard fescue, and highlight fescue. Both the size (width) of the straw stalk and the color of the particles contribute to these differences.

Differences in wax content might also contribute to differences in physical properties, since it has been shown that the removal of wax from the surface of the straw particle improves the strength of straw particleboard (see Figure III. B. 2.).

Particle Size The straw particle size can be reduced by passing the straw through a mill; the average particle size being determined by the size of the holes in the screen.

Straw particleboard strength is directly affected by particle size because small particles, having more surface area, tend to pack more tightly and collect more resin, while the tensile strength of longer particles is also a factor.

Differences in the handling characteristics of straw particles have also been noticed; short particles flow more easily than longer particles, but produce a board of lower strength.

Moisture Content   Moisture content is an important variable for two reasons; the reaction of water with the isocyanate resin, and the vaporization of the water during the pressing cycle.

Although no direct measurements have been made, there is no apparent detrimental effect on the board physical properties by the presence of a small amount of water in the straw, that is, strong boards can be produced whether the water is removed prior to application of the resin or during the pressing operation itself, however, the temperature profile of the board in the press will be different in the two cases. In addition, it is presumed that any water in the straw would react with the resin over a period of time if the resin-straw mixture were being stored prior to utilization.

Any gas that is produced in the board during the pressing operation must be allowed to escape prior to releasing the pressure or delamination (blows) will occur.

Resin   Three variables involving the resin may affect the board physical properties; resin type, resin concentration, and resin application method.

A variety of isocyanate resins are available industrially including 4,4'-diphenyl methane diisocyanate, polymethylene polyphenylisocyanate, tolylene 2,4-diisocyanate, hexamethylene diisocyanate, and m-xylylene diisocyanate. The reaction rates of these compounds with cellulose and with water are unknown, however, straw particleboards have been made in the laboratory with tolylene 2,4-diisocyanate (with dibutyltin diacetate catalyst), 4,4'-diphenylmethane diisocyanate, and polymethylene polyphenylisocyanate.

Resin concentration should have a direct effect on the board physical properties, unless the breaking strength is determined by other factors such as the internal cohesion of the straw particle. Although the effect of changes in resin concentration on board physical properties has not been completely evaluated, preliminary tests have shown that the board strength increases as the resin concentration increases.

The technique of resin application will affect the distribution of the resin on the straw particles. Lehmann (12) has shown that the distribution of resin is the most important factor in the strength and stability of wood particle boards. He has also shown that fine atomization of the resin and a suitable period of application were the most important factors controlling optimum distribution of resin.

The isocyanate resins that have been used in this study are viscous liquids which can be applied by air aspiration and dispersion. A solvent can also be used to reduce the resin viscosity and improve the atomization, but boards produced in this manner do not have the strength of those made with the undiluted resin.

A uniform application of resin could also be attained by soaking the straw in a solvent solution of the resin.

Pressing The straw-resin mixture forms a solid board when it is subjected to heat and pressure for an adequate length of time. Variables in the pressing operation include pressing time, pressing temperature, pressure, and speed of closing. Although the speed of closing can be adjusted to change the ratio of the modulus of rupture to the internal bond in a wood particleboard process, no evaluation of this variable has been made in this study.

Pressing time is measured from the time the press reaches maximum pressure, or from the time the press is closed if stops are used. The time must be long enough for the center of the board to heat up and complete the reaction, but should not be too long because degradation may occur. Preliminary studies have shown that board strength increases with an increase in pressing time up to a point, and then decreases. The optimum pressing time is determined by the pressing temperature.

The effect of pressing temperature on the physical properties of the straw particleboard has not been determined, but will affect the temperature profile within the board and the degradation rate of board components. The temperature must be high enough to allow the reaction to be completed, but should not be too high because the straw will undergo thermal decomposition. Preliminary tests have shown that the range of allowable temperatures is 250-400°F, with 325-350°F being most desirable.

The pressure exerted on the straw particles will determine the thickness and density of the resulting board unless stops are used. An increase in pressure results in a decrease in thickness and an increase in density. When stops are used the pressure is no longer a variable, as long as the press can be closed, and the density will be determined by the amount of straw being used, and the thickness will be determined by the stops. However, a higher density board will require a higher pressure for closure, and the effects of higher pressure on physical properties can be measured in terms of the effects of higher density. In general, the strength of a straw particleboard increases as the density increases regardless of whether the thickness or the weight of the board is held constant.

Finishing The finishing operations that are required will depend on the techniques being used in the pressing operation. If the boards are pressed in a mold, the edges will be firm and no trimming will be required; however, if the boards are pressed with unrestrained edges, they will be soft and will need to be trimmed. In addition, it may be desirable to provide the board with a paint, lacquer, or vinyl finish.

Experimental Results: Three sizes of straw particleboard samples have been prepared for evaluation, a laboratory test sample measuring 4 1/2 inches by 4 1/2 inches, a standard test sample measuring 12 inches by 12 inches, and a commerical test sample measuring about 4 feet by 8 feet. All of these samples were prepared from baled straw that had been stored in an open shed for at least six months. The results of these tests are listed below.

Laboratory Test Samples These samples were prepared using a manually operated, heated-platen (5 inch by 8 inch), hydraulic press and a 2-piece mold designed to produce a 4 1/2" x 4 1/2" x 3/8" board. Although these samples were too small to allow the use of ASTM standard testing procedures for the determination of physical properties, non-standard tests were used to show differences rather than absolute values.

The Modulus of Rupture (MOR) is influenced by the board density as shown in Figure III. B. 3. These samples were prepared at 350°C using 3% isocyanate resin. This straw was milled on a hammermill with 1/4" screen and was dried prior to the resin application. The optimum pressing time for these conditions is five minutes. The MOR increases with increasing density.

Figure III. B. 4. shows the effect of pressing time on MOR for samples prepared at 340°C using 3% isocyanate resin. This straw was milled on an Abbe mill with 3/16" screen and was dried prior to the application of the resin. The optimum pressing time for these conditions is two minutes or less, and again the MOR was higher for the boards produced with higher density.

Figure III. B. 5. shows the effect of resin concentration on MOR for samples prepared at 300°F. This straw was milled on a hammermill with a 1/4 inch screen and was not dried prior to application of the resin. In addition, a small amount of acetone was used in the resin to lower its viscosity and the straw-resin mixture was stored in a plastic sack for about 24 hours prior to pressing. The optimum pressing time for these conditions is four minutes, except for a resin concentration of 1.25%, then it is five minutes or longer. At two minutes pressing time the optimum resin concentration is 2.0%, while for pressing times of three, four, and five minutes the optimum resin concentration is 1.5%.

The thermal conductivity of straw particleboard was determined and compared to samples of wood particleboard, asbestos, and air.

Since heat transfer through a material by conduction is governed by the Fourier equation, $\frac{d\theta}{dt} = kA \frac{dT}{dx}$ where $\frac{d\theta}{dt}$ is the rate of heat flow, A is the area of contact perpendicular to heat flow, $\frac{dT}{dx}$ is the temperature gradient through the material and k is the thermal conductivity constant for the material, the thermal conductivity constant for a test material (k) can be determined byapplying heat to one side of a stack which includes materials with known k's, and measuring the temperature gradient through the stack:

$$\frac{d}{dt} = k_t A_t \frac{(\Delta t)}{\Delta x} t = k_1 A_1 \frac{(\Delta t)}{\Delta x} 1$$

$$k_t = \frac{k_1 A_1}{A_t} \left(\frac{\Delta t}{\Delta x}\right)_1 \left(\frac{\Delta x}{\Delta t}\right)_t = k_1 \left(\frac{\Delta t_1}{\Delta t_t}\right) \left(\frac{\Delta xt}{\Delta x_1}\right)$$

Experimentally, a stack containing plates of aluminum, straw particleboard, and copper was placed in a heated platen hydraulic press. The lower platen was heated to 230°F and the top platen was held at room temperature. Pressure was applied to the stack to insure good contact between the layers in the stack. After 20 minutes the temperature profile through the stack was measured with iron-constatan thermocouples. In addition to straw particleboard, samples of particleboards made from sander dust and municipal refuse were evaluated and also samples of commercial wood particleboard, asbestos, balsa wood, air, and loose straw. The results of these tests are listed in Table III. B. 1.

The relationship between density and thermal conductivity constant is shown in Figure III. B. 6. Although no clear relationship is evident, the thermal conductivity appears to increase slightly with increase in density. A more significant factor appears to be the classification of the straw. At approximately the same density, the thermal conductivity increases as the particle size increases, with the exception of the fines. However, the boards with the lowest conductivities were prepared from heterogeneous straw with the fines removed.

Although straw particleboard seems to be a better thermal insulator than most of the other materials measured, a comparison with insulating materials has not been computed.

The water absorption properties of several samples of straw particleboard were measured to determine if changes in processing variables affected the water absorption properties. Since this test was not conducted according to the ASTM standard, only the differences in weight and length measurements were observed. The boards used in this test were 4 1/2 inches square and about 3/8 inch thick. Weight and length measurements were made prior to and after soaking under 1 inch of water for 24 hours.

The water absorption properties of straw particleboards appear to be affected by the type of resin used, the resin concentration, the moisture content of the straw prior to pressing, and the density of the board, but not by variations in resin application procedures.

Standard Test Samples These samples were prepared using an automatic hydraulic press with steam heated platens (24 inch by 24 inch). The straw mat was hand formed between two stainless steel caul plates, 12 inches by 12 inches, and placed on the lower platen. The press closing time was about 30 seconds. The first series of samples were prepared by applying constant pressure; variations in pressure resulted in variations in the density and thickness of the boards produced. The second series of samples were prepared using stops to achieve a thickness of 3/8 inch. Variations in density were produced by variations in the quantity of straw used in the mat. The boards were trimmed to 11 1/2 inches by 11 1/2 inches, providing an adequate sample for physical testing using ASTM procedure D-1037-64. The physical properties of these test samples are listed in Table III. B. 2.

The density of the boards is determined primarily by the level of pressure applied, when stops are not used. The relationship between pressure and density is shown in Figure III. B. 7. When a constant pressure of over 1000 p.s.i. was applied for over one minute, "blows" appeared in the board. Although an alternative technique of allowing the straw mat to heat up for two minutes at 200 p.s.i. prior to application of the higher pressure prevented the "blow" formation, this technique also affected the physical properties of the boards including the density.

Board density is also affected by the pressing time. The effect of pressing time on board density is also shown in Figure III. B. 7. Time apparently has a greater effect on board density at high pressure (1000 p.s.i.) than at low pressures (200 p.s.i.).

The Modulus of Rupture is affected by the removal of wax from the straw. Figure III. B. 2. shows the effect of wax removal on MOR for three kinds of straw. The removal of wax from the straw results in a significant increase in MOR, but loss in water swell properties.

The Modulus of Elasticity (MOE) is influenced by board density as shown in Figure III. B. 8. These samples were prepared with 5% isocyanate resin. An increase in density results in an increase in MOE. Variations in Figure III. B. 8. may be caused by variations in average particle length.

The MOE is also affected by the removal of wax from the straw. Figure III. B. 2. shows the effect of wax removal on MOE for three kinds of straw. The removal of wax from the straw results in a significant increase in MOE, but this effect is not as great as the effect on MOR.

The internal bond values listed in Table III. B. 2. are not indicative of the actual strength of the boards since the separation during testing occured at the metal surface and not within the board; therefore, it is not possible to show the effects of changes in board density or thickness on the I.B.

Figure III. B. 2. shows the effect of wax removal on the I.B. for three kinds of straw. The removal of the wax results in a significant increase in the I.B.

The water absorption properties of several different materials, pressed under varying conditions are shown in Table III. B. 3. Reproducibility of results, holding all parameters constant, is indicated by samples 2 and 9. Variation of resin type produced the results shown in samples 1, 11, and 15.

As one can see from samples 5, 6, and 7, or 9 and 11, resin concentration has small influence on water absorption properties. Density also has only a small influence as shown in samples 1 and 8.

Samples 18 and 19 were cut from a single sheet of commercial wood particleboard for use as a comparison with laboratory products. Eight percent PAPI on straw gives about the same water absorption properties as the 6-8% resin used in the wood counterpart as can be seen by comparing samples 18 and 19 with samples 2 and 9.

The samples made from paper were inferior, possibly because of the lack of wax "sizing". Sizing is added to wood particleboard, but because of the natural wax in straw there is no need to add sizing to straw particleboard.

In general one can summarize by noting that increased density and increased resin concentration reduce the swell caused by water absorption in straw particleboard. The polyisocyanate resin, Mondur MRS, appears to give slightly better moisture stability characteristics than the other resins tested. Paper might be used as a fiber source if wax is added to decrease the water absorption.

Commercial Test Samples Two commercial samples were prepared in a 5 foot by 9 foot multi-opening press to evaluate the engineering factors involved in industrial production of full sized sheets (4 foot by 8 foot). The straw was milled in a hammermill with screen openings larger than 1/2 inch diameter, and was dried in a tray drier at 65°C for 24 hours. The isocyanate resin was applied at 5% to 1600 gram batches of straw, and the mixture was stored in plastic bags for 24 hours prior to pressing. Approximately 35 pounds of treated straw were used in each board.

The straw mat was hand formed on an aluminum caul plate and the plate was lifted onto a conveyor belt for feeding into the press. Paper was used on the top and bottom of the mat to prevent sticking to the platens. The platens were heated to about 325°F and the pressing time was about 5 minutes. A constant pressure of over 1000 p.s.i. was applied.

When the pressure was released, the boards delaminated severely, although the two layers appeared to have good cohesion. Wide variations in thickness were observed; this resulted from the hand forming operation. The straw does not flow readily and is difficult to form into a uniform mat. The paper that was used stuck to the straw particleboard on both sides but most of it could by removed by soaking it with water and scraping it with a spatula. The soft edges were trimmed and the resulting board showed no major defects except for the delamination. No physical properties were measured.

In order to produce full sized sheets for physical testing, a mechanical mat forming device should be used, and if resin sticking is a factor, release paper should be employed. In addition, the pressing conditions should be adjusted to prevent delamination.

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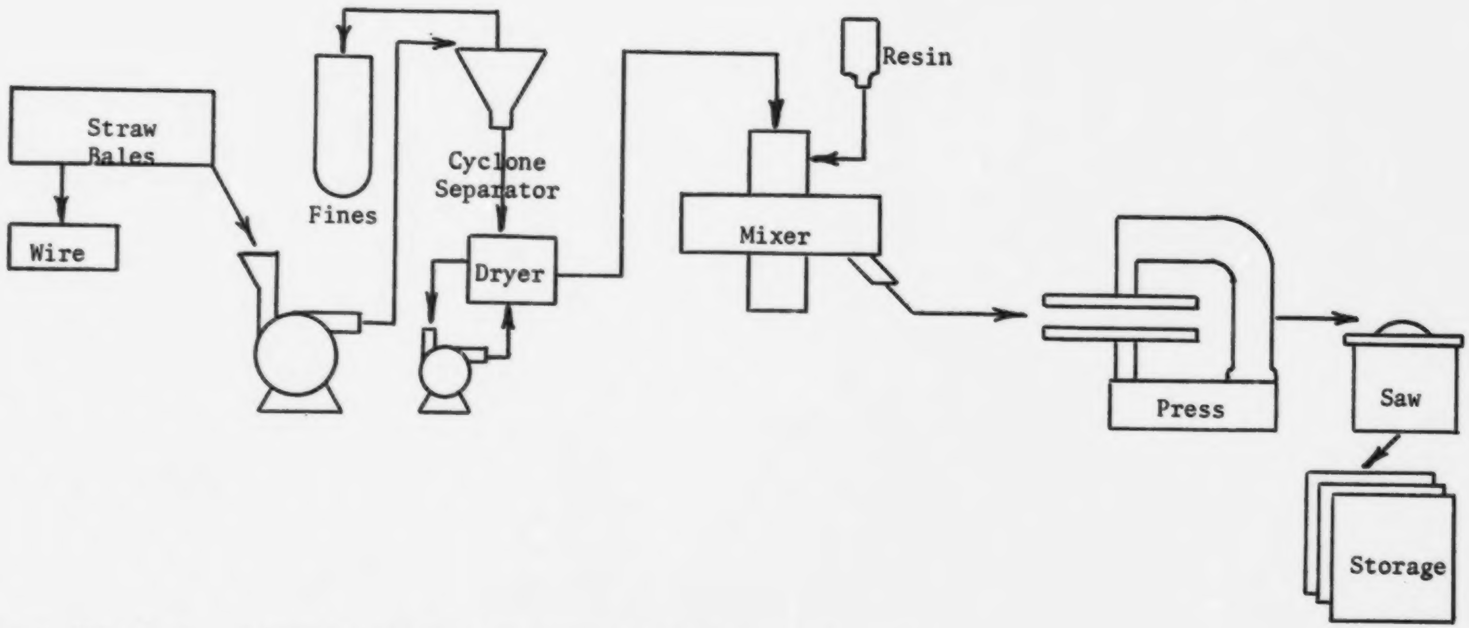

Straw Bales
Wire
Fines
Cyclone Separator
Dryer
Resin
Mixer
Press
Saw
Storage

Figure III. B. 1. Schematic Diagram for Straw Particleboard Formation.

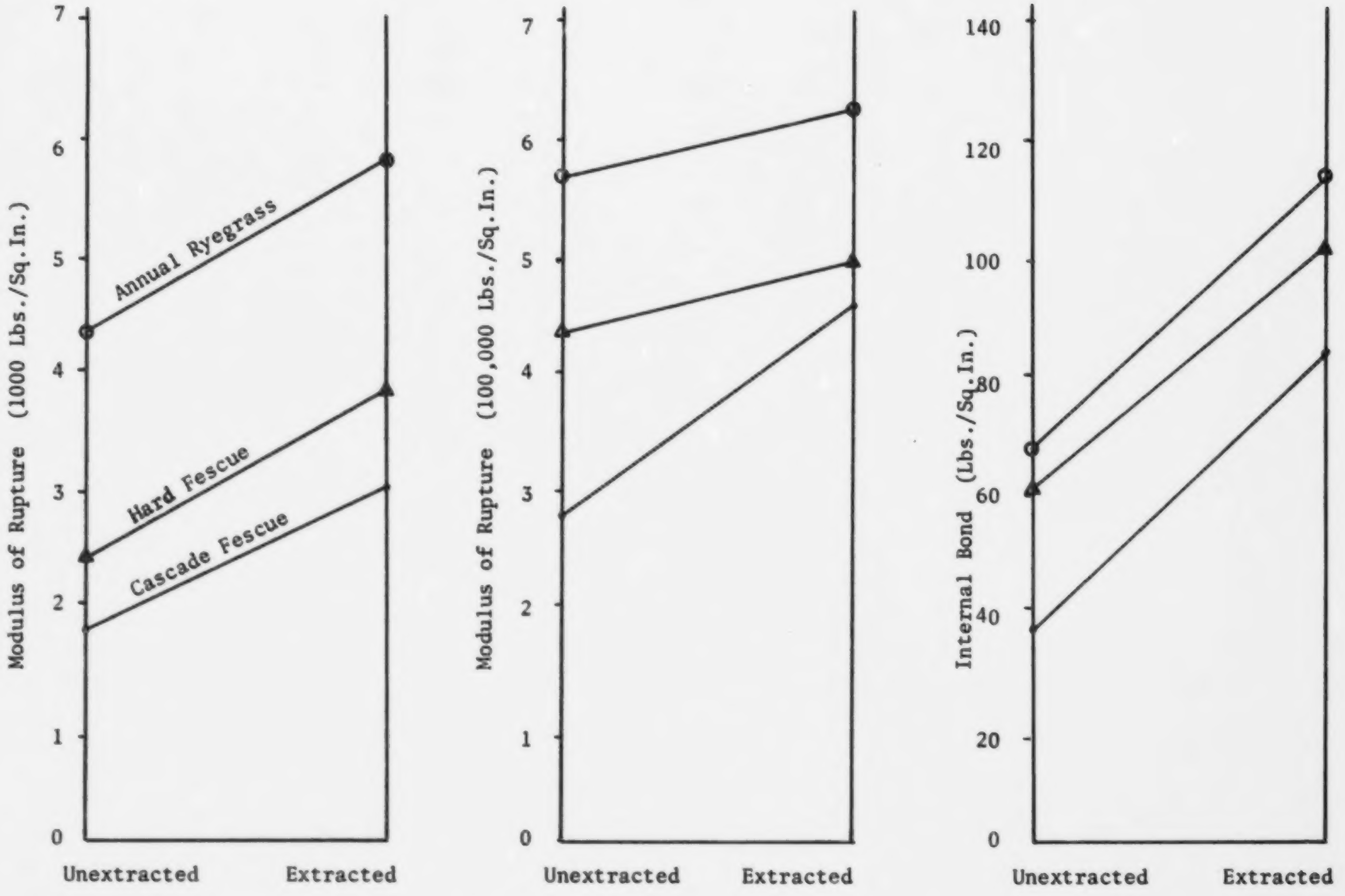


Figure III. B. 2. Effect of Wax Removal on Straw Particleboard Physical Properties.

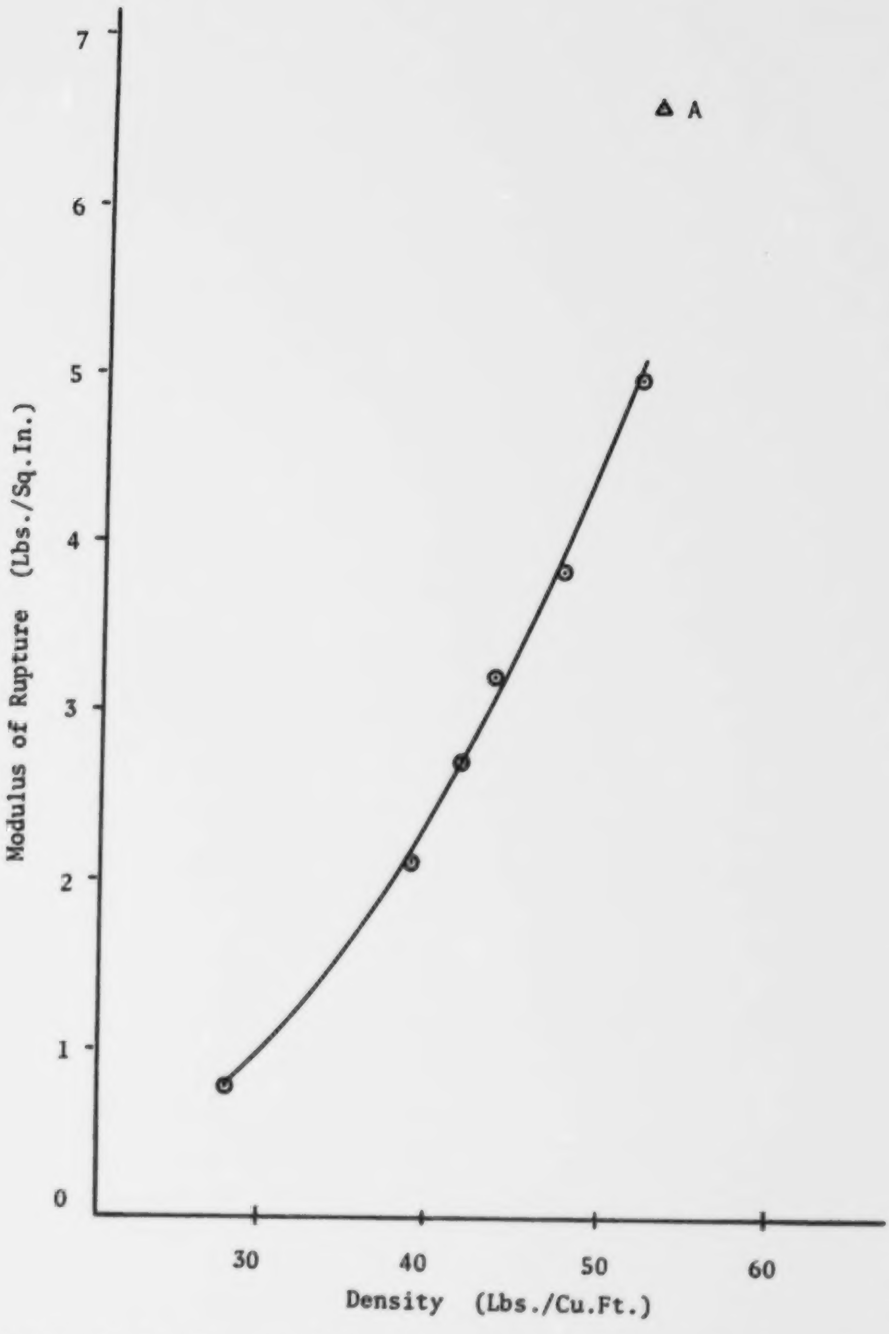


Figure III. B. 3. Increased Board Strength Brought About by Increased Density. Point A Indicates Increase of Strength Because of Longer Fibers.

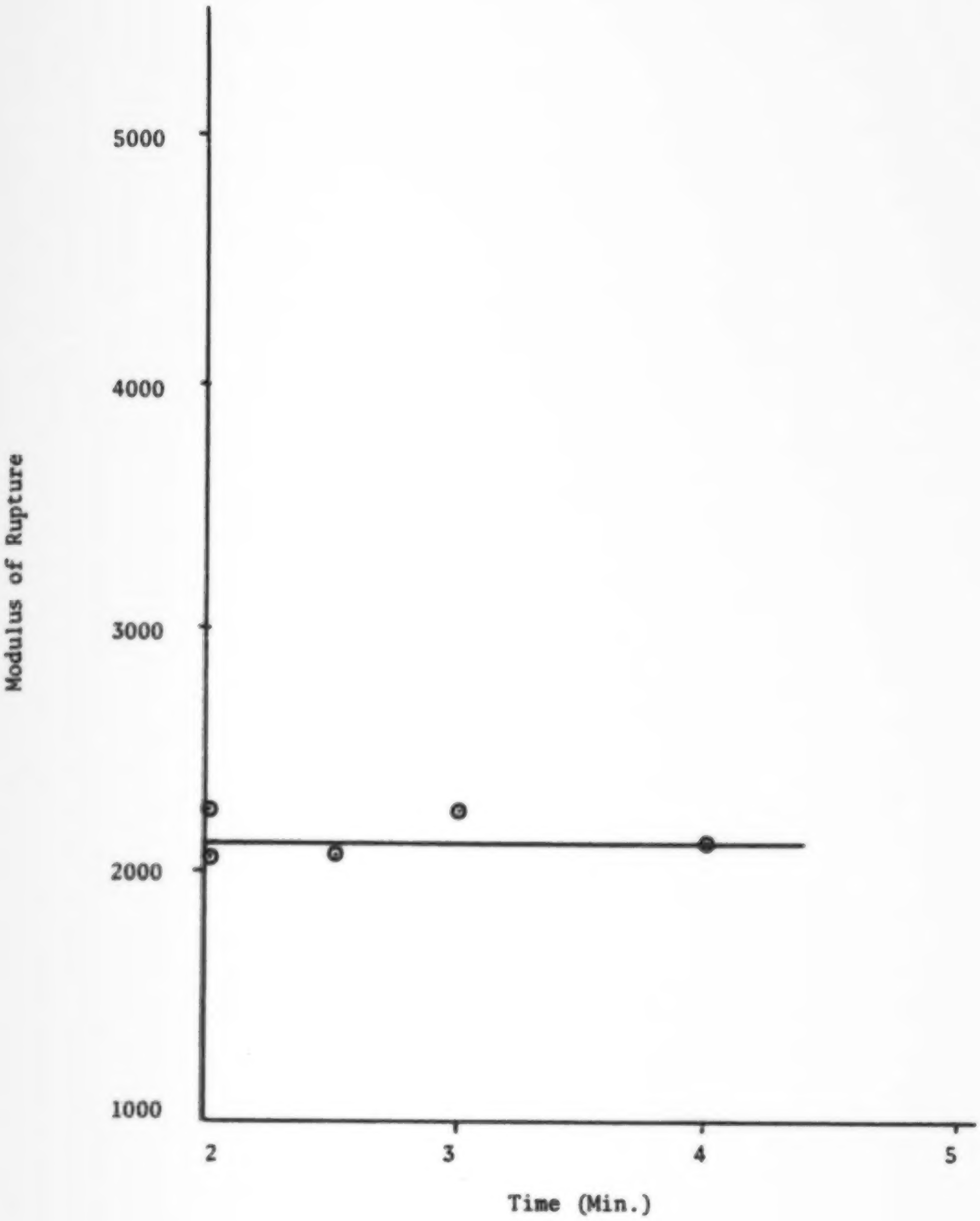


Figure III. B. 4. Effect of Pressing Time on Modulus of Rupture.

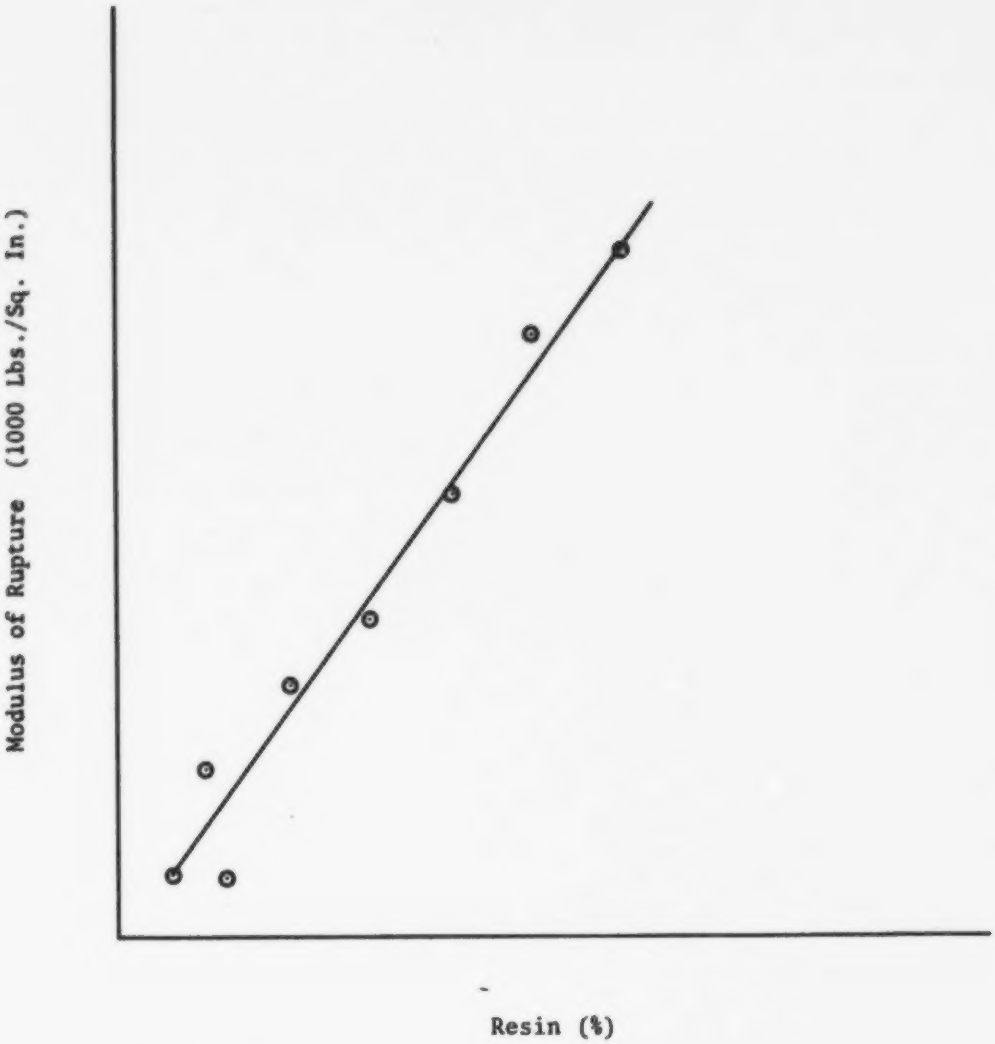


Figure III. B. 5. Increased Board Strength Caused by Increased Resin Concentration.

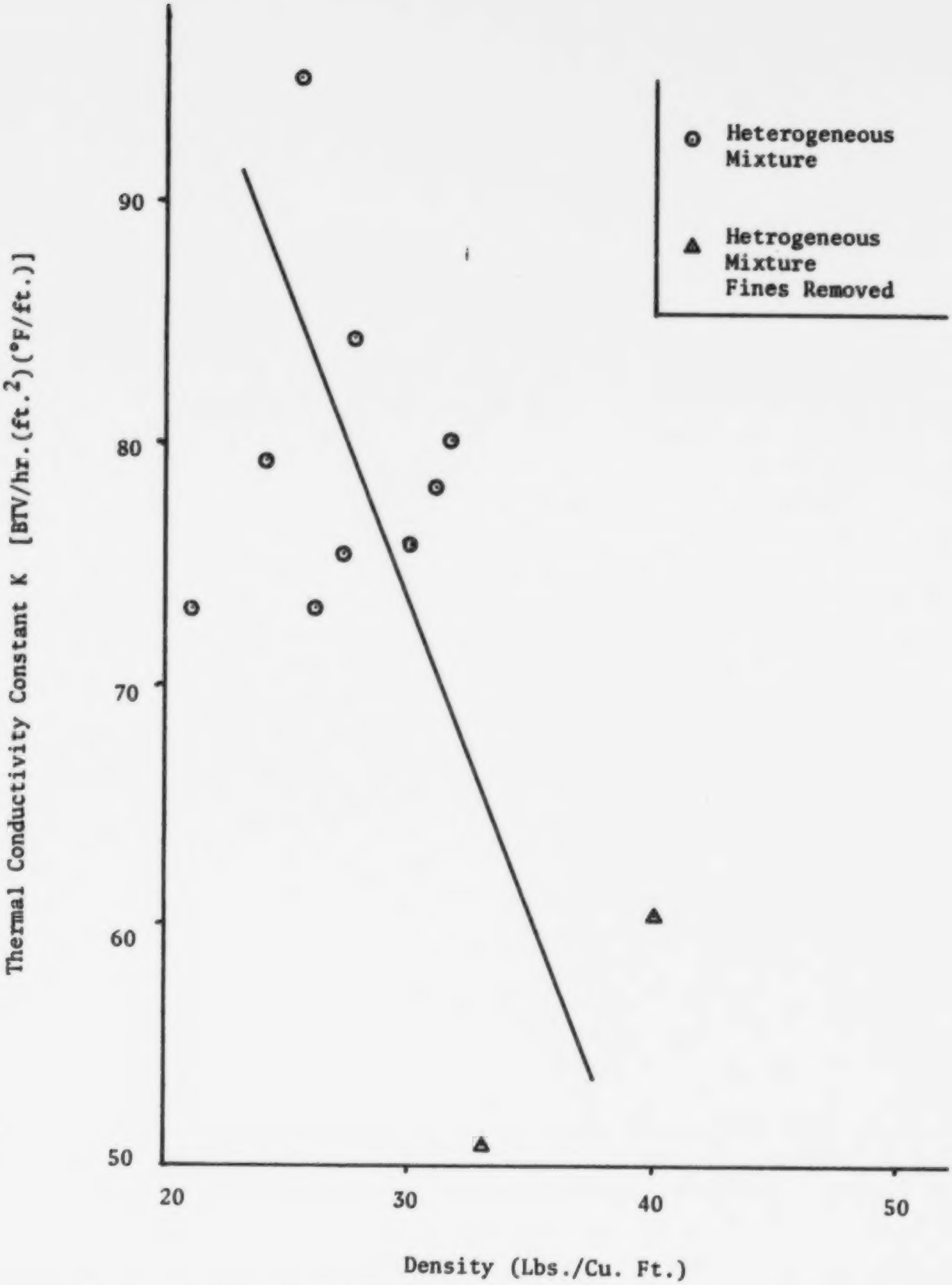


Figure III. B. 6. Relationship Between Density and Thermal Conductivity.

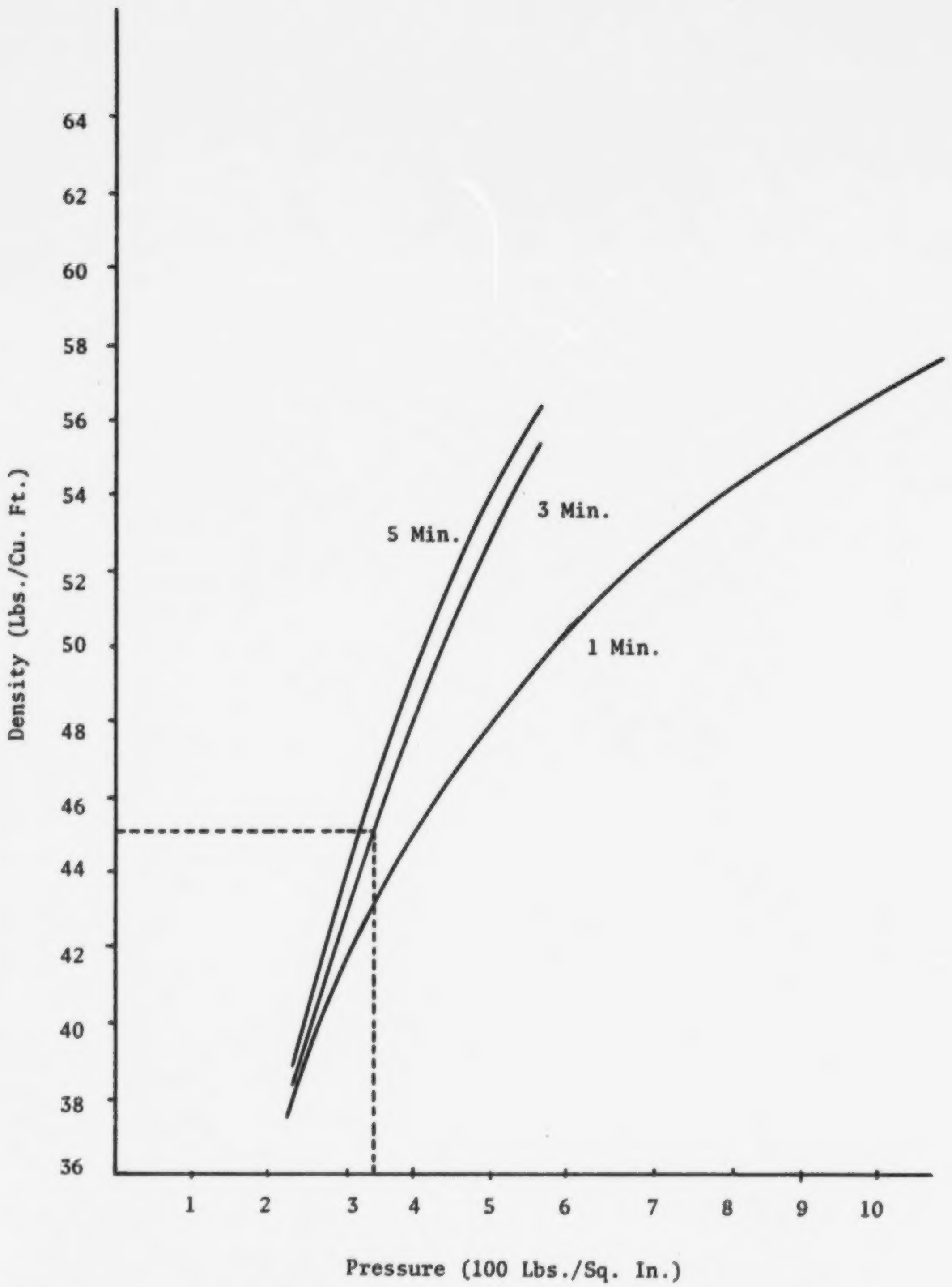


Figure III. B. 7. The Relationship Between Pressure and Density.

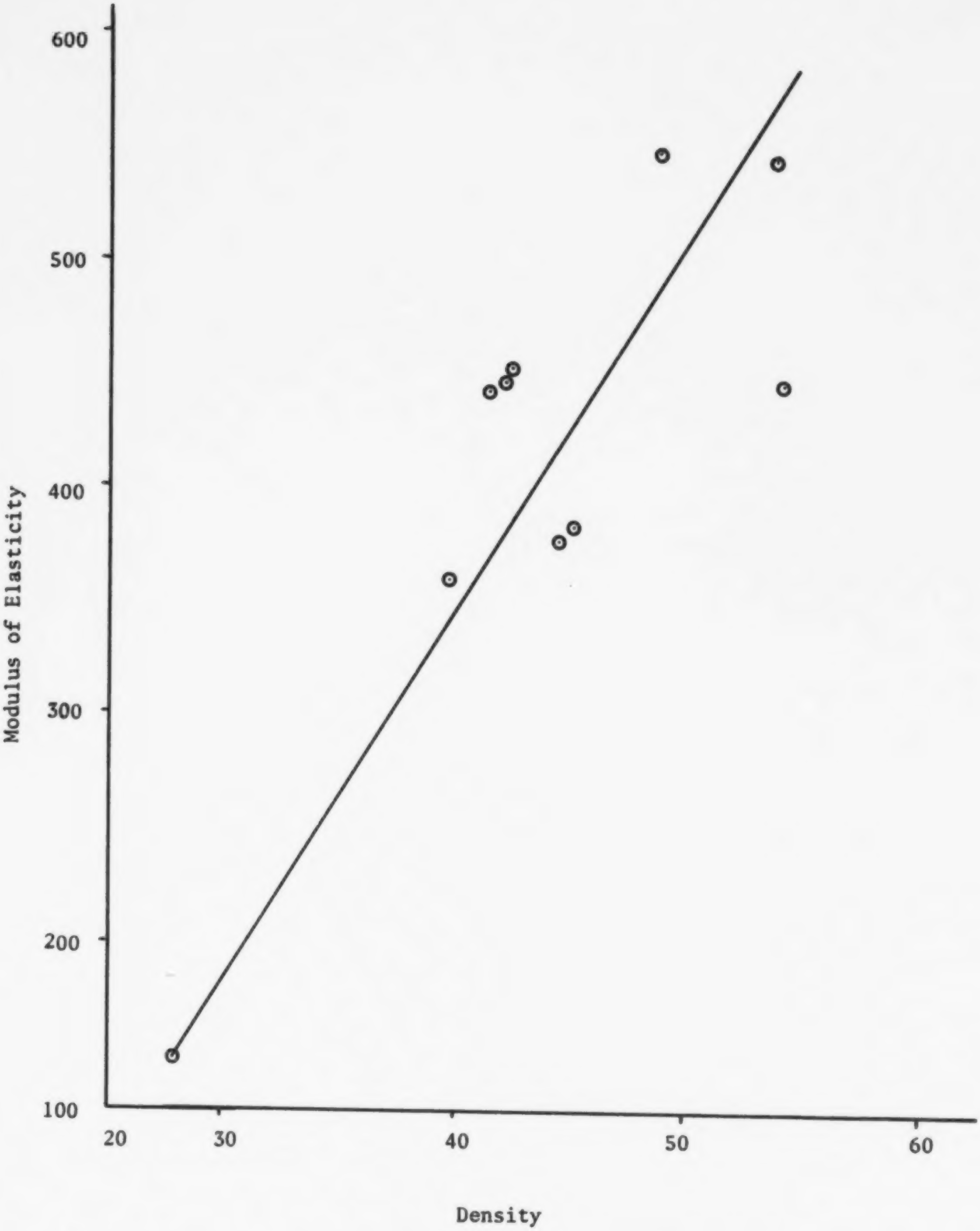


Figure III. B. 8. Showing the Influence of Density on the Modulus of Elasticity.

Table III. B. 1. Thermal Conductivity of Straw Particleboard and Other Substances

Sample	Thickness, in.	Density, lb/cu.ft.	k BTV/hr.(ft^2)(°F/ft.)
Straw particleboard, heterogeneous mixture			
1	0.247	30.0	0.76
2	0.255	27.5	0.84
3	0.231	28.2	0.76
4	0.238	25.4	0.95
5	0.232	23.8	0.79
6	0.243	20.8	0.73
7	0.259	30.8	0.78
8	0.267	31.7	0.80
Straw particleboard, classified			
Fines			
9	0.237	30.4	0.73
10	0.245	45.0	0.85
11	0.298	49.6	1.08
12	0.215	34.6	0.83
Medium length			
13	0.233	30.4	0.59
Medium/coarse length			
14	0.229	30.9	0.66
Coarse			
15	0.228	30.4	0.71
Heterogeneous, but with fines removed			
16	0.244	40.0	0.61
17	0.224	33.0	0.52
Loose straw			
18	0.360	3.7	0.78
Balsa wood			
19	0.225		0.67
Commercial wood particleboard			
20	0.367		1.12
Asbestos			
21	0.250		1.20
Sander dust			
22	0.216		1.57
Municipal refuse			
23	0.294		1.72
Air			
24	0.360		1.01

Table III. B. 2. Physical Properties of Straw Particleboard

Sample[1] No.	Straw[2] Type	Temp., °F	Press., psi	Time, min.	Ave. Density, lb/ft^3	Ave. Thickness, in.	MOR, psi	MOE, 1000 psi	IB,[3] psi
1 (w)	AR	344	216	1	37.4	0.220	2190	308	61 (s)
2 (w)	AR	343	216	3	37.6	0.212	2369	341	82
3 (w)	AR	344	216	5	37.8	0.208	2276	338	84
4 (w)	AR	345	540	1	48.1	0.173	4520	545	90 (s)
5 (w)	AR	347	540	3	54.9	0.141	5680	672	130 (s)
6 (w)	AR	346	540	5	55.8	0.148	6892	780	110 (s)
7 (w)	AR	344	1080	1	57.6	0.137	6740	772	88 (s)
8 (w)	AR	344	200/1080	2/1	55.0	0.148	4477	580	65 (s)
9 (w)	AR	345	200/1080	2/3	58.2	0.137	4655	669	94 (s)
10 (w)	AR	349	200/2160	2/1	61.3	0.132	5375	718	66 (s)
11 (w)	AR	344	200/2160	2/3	63.8	0.133	2696	746	94 (s)
12 (w)	AR	340	216	1	37.2	0.149	2621	367	68
13 (w)	AR	358	216	3	39.7	0.135	3642	341	98 (s)
14 (w)	AR	346	216	5	40.7	0.136	2990	443	80 (s)
15 (w)	AR	350	216	1	36.4	0.069	2603	364	
16 (w)	AR	354	216	3	37.4	0.070	3588	434	
17 (w)	AR	354	216	5	41.0	0.066	5818	607	
18 (w)	AR	325	stops	4	44.5	0.333	4318	626	103
19 (u)	AR	325	stops	4	44.3	0.334	3873	565	61
20 (w)	HF	325	stops	4	44.3	0.335	2408	498	116
21 (u)	HF	325	stops	4	43.8	0.336	3156	438	68
22 (w)	CF	325	stops	4	44.7	0.337	1662	450	80
23 (u)	CF	325	stops	4	36.4	0.331		258	32

1 (w) means extracted, (u) means unextracted
2 (AR) means annual ryegrass, (HF) means hard fescue, (CF) means cascade fescue
3 (s) means surface failure

Table III. B. 3. Changes in Weight and Linear Dimensions of Boards Made From Various Materials When Soaked in Water for 24 Hours.

	Substance	Treatment	Resin		Density	Dimensional Change	
			Type	Wt. %	Dry (g/cc)	Length %	Weight %
1	Straw	Dried 110°C/15 hr.	PAPI	5.5	0.81	0.866	58
2	Straw	Field run (9% H_2O)	PAPI	8	0.98	0.347	28
3	Paper	Ground & dried	PAPI	8	0.66	0.435	46
4	Sanderdust		PAPI	3	0.65	2.34	46
5	Sanderdust		PAPI	4	0.68	2.34	42
6	Sanderdust		PAPI	5	0.71	2.34	36
7	Straw	Abbe treated	PAPI	5	0.82	0.868	49
8	Straw	110°/15 hr.	PAPI	5	0.66	0.866	56
9	Straw	Field run (9% H_2O)	PAPI	8	1.01	0.347	30
10	Paper	Ground & dried	PAPI	8	0.66	0.435	33
11	Straw	Air dry after spray	P-F	5	0.99	1.04	67
12	Straw		PAPI	10	0.94	0.433	22
13							
14							
15	Straw	Air dry 65°C	MRS	5	0.62	0.86	37
16	Straw	110°/15 hr.	MRS	5	0.60	0.605	25
17	Straw	Air dry 65°C	MRS	5	0.69	0.605	38
18	Wood particle	Commercial			0.63	0.343	43
19	Wood particle	Commercial			0.64	0.343	34

Nitrogen and Phosphorus Enrichment

The use of solid wastes as soil conditioners and fertilizers is hindered by their low concentration of plant nutrients, especially nitrogen, phosphorus, and potassium. Since the soil is an ideal location for the disposal of large quantities of solid wastes, it seems reasonable to consider enriching solid wastes with plant nutrients in order to make land disposal more attractive. For wastes containing large amounts of cellulose this can be done chemically by preparing cellulose derivatives that contain nitrogen, phosphorus, and potassium. The water-holding capacity of these organic materials, their insolubility in water, and their slow rate of degradation would be additional desirable characteristics. Since nitrogen and phosphorus are the two main plant nutrients required, this report will be limited to consideration of these. Potassium can be added to some cellulose derivatives which have ion exchange properties.

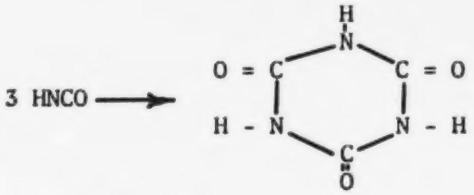
Chemistry: Many cellulose derivatives can be produced which contain nitrogen and/or phosphorus. A more extensive discussion of the chemistry involved in their formation entitled "Cellulose Compounds Containing Nitrogen" (2), can be found in a report prepared by J. F. Barbour; however, the present report will be limited primarily to consideration of the cellulose-urea and cellulose-phosphoric acid reactions.

Nitrogen Enrichment Cellulose derivatives containing nitrogen can be prepared by reacting cellulose with urea, ammonia, or nitric acid. In each case the concentration of nitrogen in the product will depend on the extent of the reaction.

Urea reacts with cellulose under the influence of heat. Extensive research on the cellulose-urea reaction has been conducted by the textile industry for the purpose of improving the crease resistance of cotton fabrics. When a mixture of urea (I), cellulose and a catalyst are heated, the product contains chemically fixed (water insoluble) nitrogen, presumably in the form of cellulose carbamate (II), as shown in reaction 1:

$$\text{Cell-OH} + \underset{\text{I}}{NH_2CONH_2} \xrightarrow{CuCl_2} \underset{\text{II}}{\text{Cell-OCONH}_2} + NH_3 \qquad [1]$$

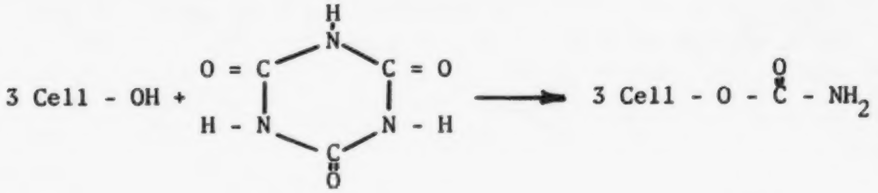
When this reaction is conducted in a closed chamber, the nitrogen content of the product is very low, indicating that the reaction is inhibited. Nuessle (8) concludes that the urea decomposes into cyanic acid (HNCO) and ammonia (NH_3) and that the ammonia must be removed in order for the reaction to proceed; however at low temperatures cyanic acid (III) can trimerize to form cyanuric acid (IV), as shown in reaction 2:



[2]

III IV

which can react with cellulose to form the cyanic acid ester (V) as shown in reaction 3:



[3]

IV V

Ammonia, under heat and pressure will react with cellulose to form "amino cellulose" as shown in reaction 4:

$$\text{Cell-OH} + NH_3 \rightarrow \text{Cell-}NH_2 + H_2O \qquad [4]$$

VI

"Amino" cellulose has been studied in relation to its fertilizing properties by Davis, et.al. (4), who describes the conversion of ammoniated peat to usable nitrates in the soil. They indicate that the amount of nitrogen available is a function of the temperature at which the cellulose-ammonia reaction takes place and that some of the nitrogeneous materials formed are soluble in water and some are not.

When cellulose is soaked in anhydrous liquid ammonia, the fibers are swollen and remain swollen when the ammonia is removed by heating at 105°C. X-ray diffraction studies (3) have shown that the ammonia is not bound to the cellulose at regular intervals and presumably amino cellulose is not formed.

Anderson (1) reports that mineral acids, such as 8.25% sulfuric acid, can be used to hydrolyze the hemi-cellulose before reaction with ammonia. When hydrolyzed cellulose was treated with ammonia at a temperature slightly above room temperature, the product contained 7.4% nitrogen which was 84% water soluble. When the hydrolyzed cellulose was treated with ammonia at 249°C the product contained 9.5% nitrogen which was 17.6% water soluble. When the reaction temperature was raised to 300°C, the product contained 4.6% nitrogen, none of which is water soluble. The product of the low temperature reaction was nearly as good as ammonium sulfate when used as a fertilizer, but the other products had a lesser effect on plant growth.

Nitric acid will react with cellulose to produce nitrate (VII) as shown in reaction 5:

$$\text{Cell-OH} + HNO_3 \xrightarrow[H_2SO_4]{} \underset{\text{VII}}{\text{Cell-ONO}_2} + H_2O \qquad [5]$$

Complete nitration of the cellulose molecule results in cellulose trinitrate. Cellulose nitration can be achieved with a mixture of nitric and sulfuric acids, nitric and phosphoric acids, nitric acid and acetic anhydride, or nitric acid and methylene chloride. When sulfuric acid is used, the process is very rapid with most of the reaction occurring in the first few minutes because the nitric acid readily penetrates into the cellulose micelle.

Cellulose nitrates can be modified to produce carboxy-cellulose nitrates, cellulose nitrosyl sulfates, and cellulose nitroethyl ethers.

Cellulose nitrates are extremely flammable, and when confined, are considered explosives. They are used in the manufacture of smokeless powder and rocket propellants as well as in plastics, films, and lacquers.

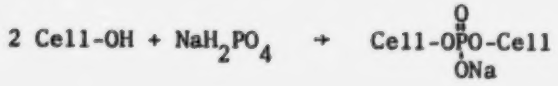
Phosphorus Enrichment When cellulose is treated with phosphoric acid, the ester cellulose phosphate (VIII), is produced as shown in reaction 6:

$$\text{Cell-OH} + H_3PO_4 \rightarrow \underset{\text{VIII}}{\text{Cell OPO(OH)}_2} + H_2O \qquad [6]$$

Nikitin (7) claims that two reaction products are possible with cellulose and phosphoric acid, one being an addition product that is easily hydrolyzed by water and the other being the ester which is unaffected by water, consequently, phosphorus fixation can be determined by measuring the phosphorus concentration of the reaction product after washing with water.

Cellulose derivatives containing phosphorus can also be prepared by reacting cellulose with ammonium phosphate, phosphorus tri- and oxychlorides, monophenyl phosphate, phosphorus pentoxide, and alkali-metal salts of phosphoric acids.

Gallagher (5) reports that sodium phosphate acts as a crosslinking agent forming dicellulose phosphate (XIX) as shown in reaction 7:

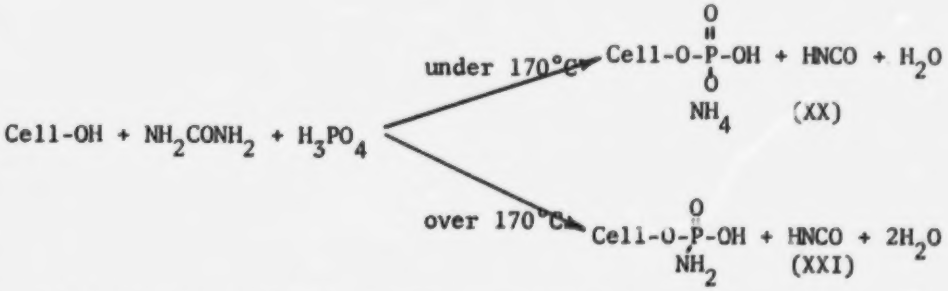


$$2\ \text{Cell-OH} + NaH_2PO_4 \rightarrow \text{Cell-O}\overset{O}{\underset{ONa}{P}}\text{O-Cell} \qquad [7]$$

XIX

The addition of phosphorus to cotton cloth has been studied extensively by the textile industry in order to achieve a flameproofing property. An extensive summary of the chemistry and uses of fire retardants is given by Lyons (6).

Nitrogen and Phosphorus Enrichment When cellulose is reacted with a mixture of urea and phosphoric acid, the product is cellulose ammonium phosphate (XX) or cellulose amide phosphate (XXI), depending on the reaction temperature, as shown in reaction 8:


Cell-OH + NH2CONH2 + H3PO4
under 170°C
Cell-O-P(=O)(ONH4)-OH + HNCO + H2O
(XX)
over 170°C
Cell-O-P(=O)(NH2)-OH + HNCO + 2H2O
(XXI)

Since cellulose phosphate has ion exchange properties, other cations can be added to the compound, such as potassium, iron, or calcium.

Process: A schematic diagram of the process is given in Figure III. C. 1.

The solid waste containing cellulose is milled to reduce the particle size and then soaked in a water solution of the appropriate reagents. If only nitrogen enrichment is desired, the solution will contain urea and a catalyst, probably cupric chloride. If both nitrogen and phosphorus enrichment are desired the solution will contain urea and phosphoric acid. After soaking, the excess solution is removed by filtration. The wet mixture is dried and then heated to the reaction temperature. Following the reaction, the product is washed with water to remove any water soluble product or unused reactants. The product is then dried and stored. A discussion of some of the variables in the process is given below.

Solid Waste Any solid waste containing cellulose could theoretically be used in the process to produce a nitrogen and/or phosphorus enriched product with fertilizing properties; however, the nature of the impurities will affect the efficiency of the reaction, for example the fillers, sizing, wax, and ink that are added to paper used in magazines may reduce the availability of cellulose hydroxyl units for reaction.

Milling Of The Waste Solid wastes can be milled to reduce the particle size for easier handling and to increase the available surface area for chemical reactions. Milling can be accomplished by use of a number of pieces of equipment such as hammermills, shredders, raspers, and hydropulpers.

Soaking In The Reagent Solution The soaking step is designed to produce a uniform mixture of the reactants, and although water is the common solvent, other solvents might be used. Although the time required for complete mixing is not great, chemical reactions during this step may affect the concentration of reagents in the cellulose after pressing. Since the solvent mixture can be recycled, the amount of chemicals and solvent added each time will equal the amount of chemicals and solvent entrained in the cellulose.

This process could be a batch or continuous operation.

If uniform mixing of the reactants with the cellulose is not required, such as would be the case if the reaction were vapor phase, then soaking and filtering would not be required.

Filtering To Remove Excess Reagents The excess solution can be removed from the cellulose by filtering, filter pressing, or by centrifuging, depending on which method provides the best wet/dry ratio. When this ratio is high, more heat will be required to remove the solvent. The reactant concentration in the solvent will have to be adjusted in order to attain the appropriate concentration of nitrogen and phosphorus in the cellulose.

Drying To Remove The Solvent The purpose of this step is to remove the excess solvent carried along in the cellulose. Although this step could be included in the first part of the heating step, it may be desirable to recycle the solvent or to collect a component of the reaction gases. Pre-drying will allow a better measure of the actual reaction time, but reactions may also occur at the drying temperature. Drying, if it is used, can be accomplished in a variety of ways, such as tray, rotary drum, vacuum, and radiant heat drying.

Heating To Promote The Reaction This step provides the temperature for completion of reaction. The reaction temperature and reaction time will probably both affect the speed and extent of the reaction These factors will also have an effect on the degradation rate of the organic components of the waste, which may influence the physical and chemical properties of the product.

Washing To Remove Unreacted Materials When a water-insoluble product is desirable, washing will be required, after the reaction is completed, to remove unused reagents and water soluble reaction products. These compounds can be recovered for reuse by drying, or the water solution could be reused in the soaking operation. In actual practice, it may be beneficial to leave some water soluble plant nutrients in the final product to provide an immediate stimulus to the plant growth. The fixed nutrients would then become available as the enriched cellulose slowly degraded.

Experimental Results: In the laboratory, samples of newspaper and straw have been treated with ammonia, nitric acid, urea, and phosphoric acid to give products with varying concentrations of nitrogen and phosphorus. Several different techniques were used for mixing and heating the reactants. Nitrogen and phosphorus concentrations were measured before and after water washing to determine the levels of fixed nutrients in the product. Selected samples of these products were then tested in a greenhouse soil test to determine if they possessed fertilizing properties comparable to commercial fertilizers. The long range or "slow release" fertilizing properties have not been evaluated as yet.

Nitrogen Enrichment

Urea was reacted with cellulose in a series of experiments to determine the affects of changes in reaction variables on the degree of nitrogen fixation in the cellulose of newspaper.

The effect of reaction time on nitrogen fixation is shown in Figure III. C. 2. Shredded paper was soaked in a 40% solution of urea for two hours and the excess solution was removed by filtration to give a wet/dry ratio of 4.5. The wet paper was dried for 16 hours at 110°C and then divided into eight parts which were reacted at 150°C for varying times up to 17 hours. The level of nitrogen fixation increases as the reaction time increases, however, the maximum level of fixation was not determined initially. The maximum fixation possible under these conditions was later determined (Curve B) using a 50% urea solution and a 4.4 wet/dry ratio. This paper was dried at 110°C for 20 hours and then divided into eight parts. The longest reaction time was 42 hours. The maximum nitrogen concentration attained in the reaction product was about 13%. If on the average one cyanic acid molecule reacted with one anhydroglucose unit, it would produce a nitrogen concentration of 7.0%, while two cyanic acid molecules/anhydroglucose unit would result in a nitrogen concentration of 11.3%, and three cyanic acid molecules/anhydroglucose unit would result in a nitrogen concentration of 14.4%. The maximum fixation achieved, then, was on the average 2.5 nitrogen molecules per anhydroglucose unit; however it is very likely that prolonged exposure of the cellulose to the heat resulted in some cellulose degradation so the nature of the chemical bonding involving the nitrogen cannot be specified with certainty.

The catalyst cupric chloride, at 5% of the weight of urea, has a definite influence on the rate of nitrogen fixation as shown in Figure III. C. 2. The paper was soaked in a 50% urea solution for two hours and pressed to a wet/dry ratio of 4.4. The paper was dried at 110°C for

20 hours prior to being heated to the reaction temperature. Four percent nitrogen fixation was achieved during the drying operation. The rate of nitrogen fixation was initially greater than with no catalyst, but this rate decreased after about 4 hours.

The reaction temperature will affect the nitrogen fixation as shown in Figure III. C. 3. Each sample contained 25 gms. of shredded paper that had been soaked in a 19% urea solution and pressed to a wet/dry ratio of 4. The mixture was dried in the reaction flask and the reaction time was measured from the time the mixture reached the reaction temperature. Heat was applied by use of a fluidized sand bath and the flask was rotated to aid heat transfer within the flask. The reaction time for all states was 1 hour. The level of nitrogen fixation increased as the reaction temperature increased.

The urea concentration (measured as moles urea/mole cellulose) in the reaction mixture has a definite influence on the nitrogen fixation as shown in Figure III. C. 4. Each sample was prepared with 25 gms. of shredded paper soaked in a urea solution. The urea concentration was varied from sample to sample, and each sample was pressed to give a wet/dry ratio of 4. The reactions were carried out in a rotating flask heated by a fluidized sand bath. A copper chloride catalyst was used at 10% concentration (based on weight of urea) and the mixtures were heated at 190°C for 1 hour.

An increase in urea concentration resulted in an increase in nitrogen fixation, however, the 1 hour reaction time may have been the limiting factor in the 155°C curve.

Catalyst Concentration The effect of catalyst concentration (expressed as % of the weight of urea used) on nitrogen fixation is shown in Figure III. C. 5. Each state contained 25 grams of paper which had been soaked in a solution containing varying concentrations of catalyst and dried at 110°C for 20 hours. The reactions were carried out in a rotating flask heated by a fluidized sand bath.

The mixture was heated to 155°C for 1 hour. Since a nitrogen fixation of about 2% was expected with no catalyst, it appears that even small concentrations of catalyst (0.1-1.0%) have some effect on the nitrogen fixation attained, but no effect was noted for concentrations over 5%. In comparing Figure III. C. 2. and Figure III. C. 5., we find less nitrogen fixed in Figure III. C. 5. This may be caused by a lack of nitrogen available. This work needs to be re-run using greater urea concentrations.

Ammonia "Amino" cellulose was prepared from newspaper by reacting shredded paper with ammonia in a Parr high pressure bomb at elevated temperatures. The reaction temperature and pressure were varied, but it was impossible to maintain the same reaction time for all runs because of gas leaks. The results of this test are listed in Table III. C. 1.

It is not possible to know what contribution each of the variables made to the increase in nitrogen enrichment, but apparently the reaction does not proceed readily at room temperature.

Nitric Acid Nitric acid mixed with sulfuric acid was used to prepare cellulose nitrate containing 2.9%N from filter paper. No attempt was made to evaluate the effect of variables on the degree of nitrogen fixation.

Phosphorus Enrichment Four samples of straw were soaked in a 21.5% phosphoric acid solution and drained to achieve a wet/dry ratio of 4. The wet straw was heated in an oven at 100°C for 64 hours. Two samples were washed with water prior to the phosphorus concentration determination. The results are listed in Table III. C. 2. Although some phosphorylation has taken place, it is equivalent to an average of only one phosphate group per two anhydroglucose units.

Nitrogen and Phosphorus Enrichment Both nitrogen and phosphorus can be chemically fixed to cellulose by reaction with urea and phosphoric acid. Although other reactions could also be used to accomplish this, this was the only reaction used in this study. Both straw and paper were used as a source of cellulose for these reactions.

Annual ryegrass straw was soaked in a phosphoric acid/urea solution and filtered to remove the excess solution, to prepare samples with a wet/dry ratio of 4.0. The filtrate from the first sample was replenished and used for the second sample. This procedure was repeated except for the fifth sample, which was soaked in the filtrate without replenishing. The five samples were heated in an oven for 2 hours after drying. One half of each sample was washed in water. The results are listed in Table III. C. 3. On the average they contained 3.5% phosphorus and 5.0% nitrogen or 3.2 moles of nitrogen/mole phosphorus even though excess phosphorus and nitrogen were available.

Newspaper can be enriched with nitrogen and phosphorus by soaking the paper in a 40/30/30 wt./wt./wt. solution of urea/85% phosphoric acid/ water and filtering the paper to give a 4.9 wet/dry ratio. When the mixture is heated to 155°C for three hours and washed with water. The product contains 5.0% nitrogen and 4.4% phosphorus.

Some of the variables in the process which might affect the nutrient concentration are predrying, reaction time, reaction temperature, and reactant concentration.

The effect of predrying the reaction mixture on nitrogen and phosphorus fixation was determined by soaking two samples of paper in the urea/acid solution. One sample was predried for 20 hours at 110°C while the other sample was dried in the reaction chamber. Both samples were heated to 166°C for 160 minutes and then washed. The predried sample contained 6.1% nitrogen and 3.5% phosphorus while the other sample contained 5.9% nitrogen and 3.6% phosphorus. These results show that predrying the wet paper did not affect the results.

The effect of reaction time on nitrogen and phosphorus fixation is shown in Figure III. C. 6. Samples of shredded newspaper were soaked in a 40/30/30 solution of urea/85% phosphoric acid/water and pressed to a wet/dry ratio of 4.7. The reactions were conducted at 155°C in a rotating flask heated by fluidized sand bath. After washing, the nitrogen and phosphorus concentrations were determined.

Over the range used, the phosphorus concentration is not affected by reaction time, but the nitrogen concentration increased slightly with the longer reaction times.

The effect of reaction temperature on nitrogen and phosphorus fixation is shown in Figure III. C. 7. Samples of shredded newspaper were soaked in a 40/30/30 solution of urea/85% phosphoric acid/water and pressed to a wet/dry ratio of 4.0. Each sample was predried at 110°C for 16 hours prior to being heated at the reaction temperature for 1 hour in an oven. After washing, the nitrogen and phosphorus concentrations were determined.

The reaction temperature has a negligible effect on the degree of phosphorus fixation although the nitrogen fixation increased at higher temperature. Apparently most of the reaction occurred during the drying step. This is surprising considering Nuessle's suggestion that the urea (m.p. 133°C) acts as a solvent for the reaction.

The effect of reactant concentration on nitrogen and phosphorus fixation is shown in Figure III. C. 8. Samples of shredded paper were soaked in a 40/30/30 solution of urea/85% phosphoric acid/water and pressed to a wet/dry ratio of 3.0. The urea/phosphoric acid weight ratio was constant at 4/3 for each soaking solution. After predrying the mixtures were heated to 150°C for 3 hours. After washing the nitrogen and phosphorus concentrations were determined. The degree of nitrogen and phosphorus fixation increases as the reactant concentration increases, but there is obviously an upper limit to the amount of nitrogen and phosphorus that can be chemically united to cellulose.

Soil Tests These tests were conducted using No. 10 size cans filled with soil. A mixture of the various ryegrasses was used because of the response of these grasses to nitrogen in the soil. Enough commercial fertilizer or enriched waste was used to provide 50 pounds of nitrogen per acre. Approximately two weeks after the initial planting, the grass was cut to a uniform height, and the grass clippings were weighed. The grass was then cut each week for the duration of the test period. The total grass production from each state is the total of the weekly productions. All cans received the same amount of water and each can had holes in the bottom for drainage. In each series of tests, two control states were included, one with no fertilizer added and one with a sample of commercial fertilizer providing 50 pounds of nitrogen per acre.

It is presumed that when the nitrogen in the treated waste is readily available to the plant, the growth rate will be comparable to the state containing commercial fertilizer, while when the nitrogen in the treated waste is not immediately available to the plant, the growth rate will be comparable to the state containing no fertilizer. Finally when the enriched waste has a deleterious influence on plant growth, the growth rate will be less than the control with no fertilizer. The "slow release" of the treated waste was not determined by this series of tests.

The results of these tests are presented below.

Nitrogen enriched samples of waste cellulose were used in the soil tests. The tests were conducted on samples enriched with urea, ammonia, and nitric acid.

The effect of nitrogen enriched paper resulting from the reaction of urea and cellulose on plant growth is listed in Table III. C. 4. The use of the nitrogen enriched paper raised the plant growth rate slightly, on the average about 75% as much as the commercial fertilizer; however, two samples showed an exceptionally high effect, over 90% as much as the commercial fertilizers. Apparently the reaction product of the dry mixture is different than the product that results when the urea is dissolved, at least it appears to be more readily available to the plant.

The effect of amino cellulose on plant growth is listed in Table III. C. 1. Two of the samples apparently had a deleterious effect on the plant growth rate. The product that had been reacted at the highest pressure and temperature raised the plant growth rate about 40% as much as the commercial fertilizer.

The use of cellulose nitrate did not appreciably affect the plant growth rate.

The nitrogen and phosphorus enrichment influence on the plant growth rate is listed in Table III. C. 5. The use of these samples resulted in a significant increase in plant growth, on the average 130% as much as that produced by the commercial fertilizer.

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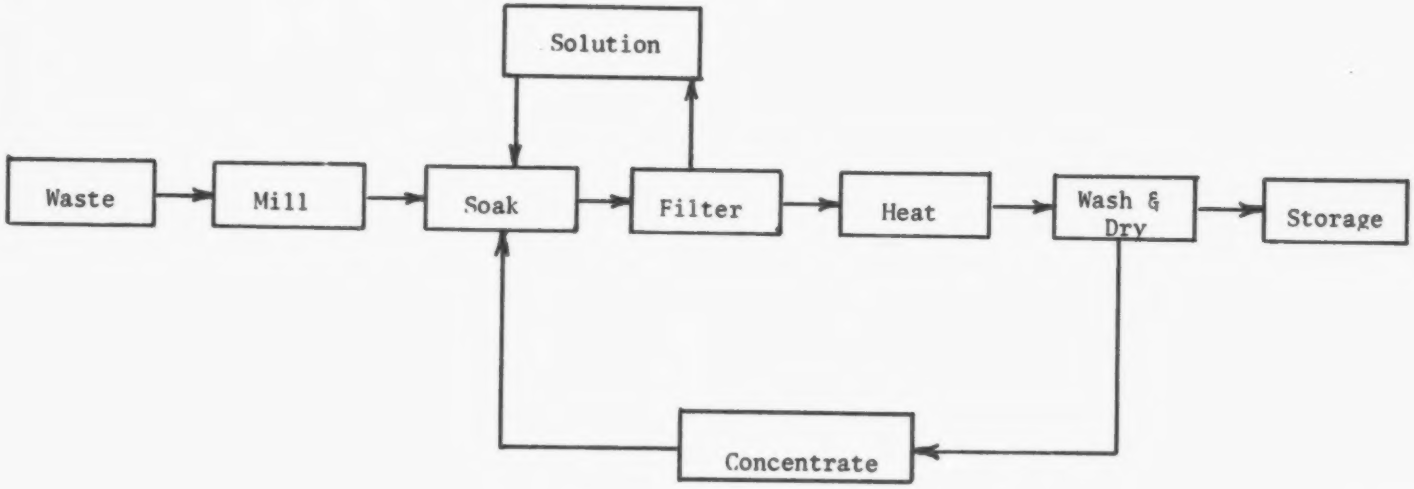

Waste
Mill
Soak
Filter
Heat
Wash & Dry
Storage
Solution
Concentrate

Figure III. C. 1. Schematic Diagram of the Nitrogen-Phosphorus Enrichment Process.

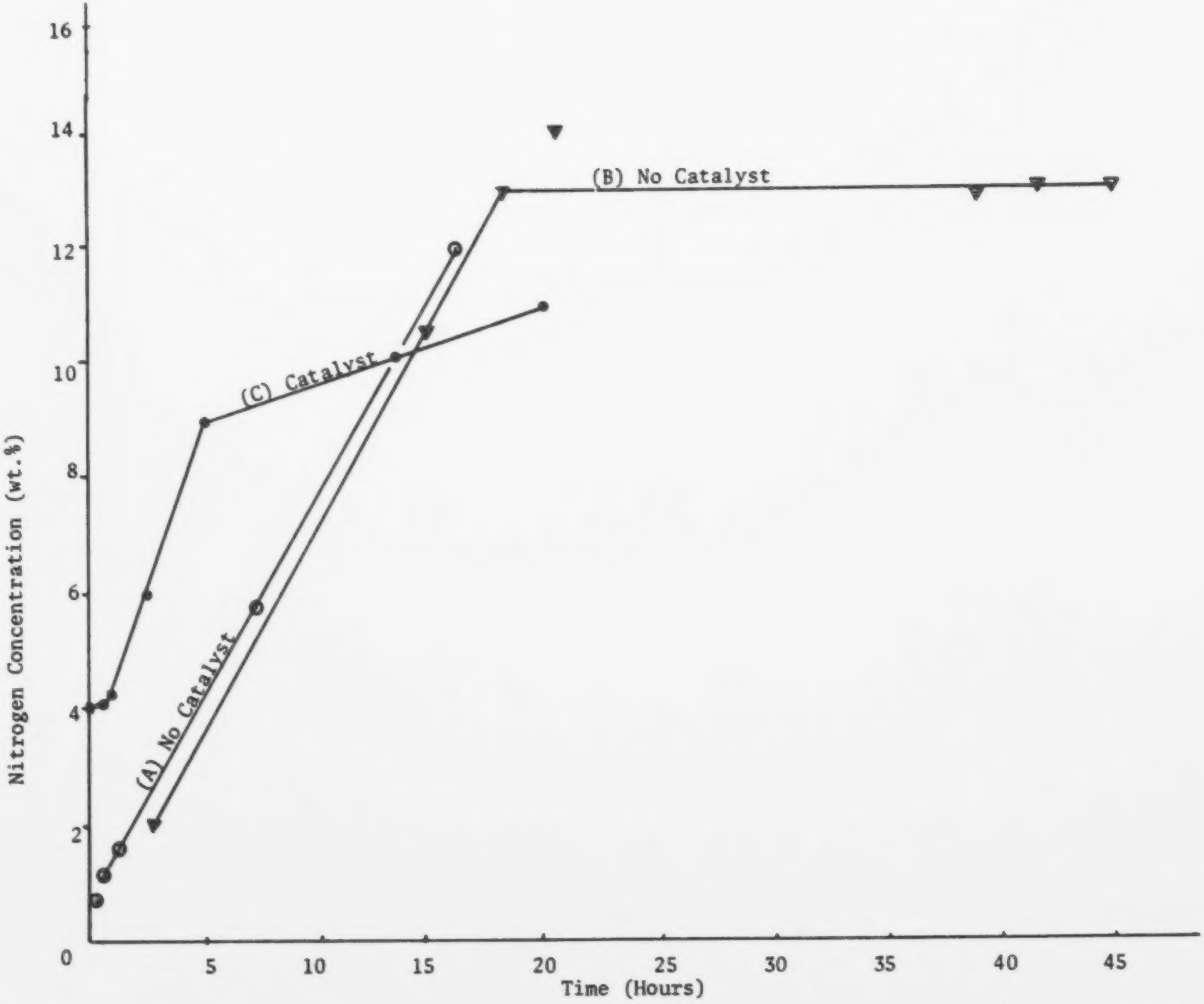


Figure III. C. 2. The Effect of Reaction Time on Nitrogen Fixation in the Reaction of Cellulose and Urea

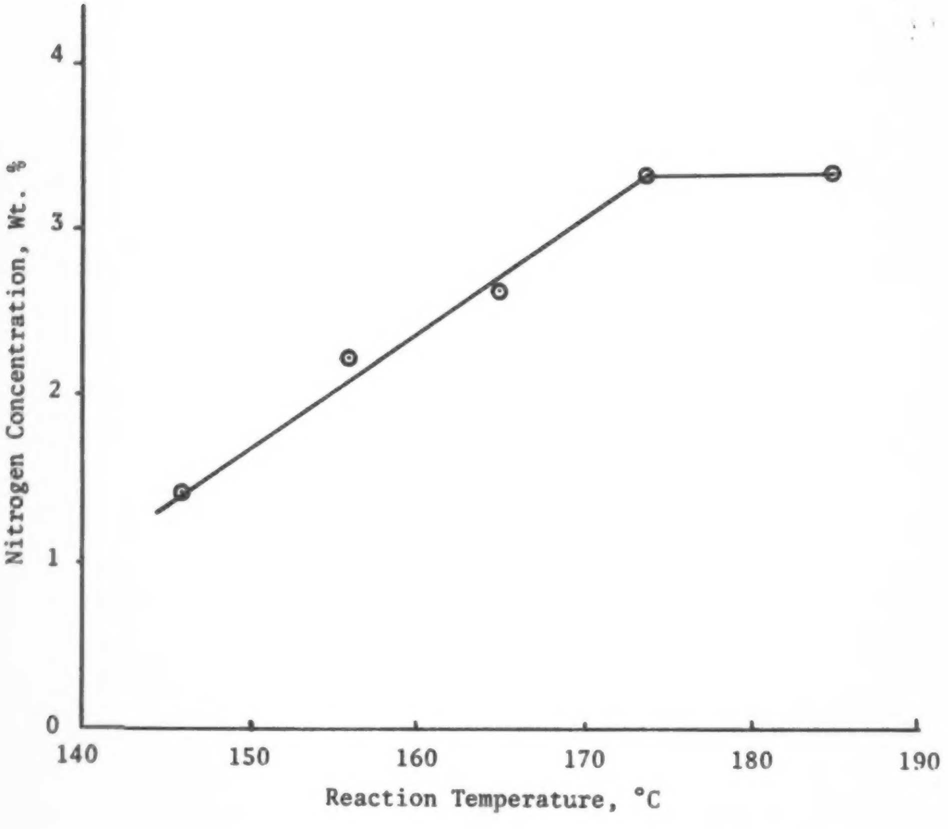


Figure III. C. 3. Effect of Reaction Temperature on Nitrogen Concentration.

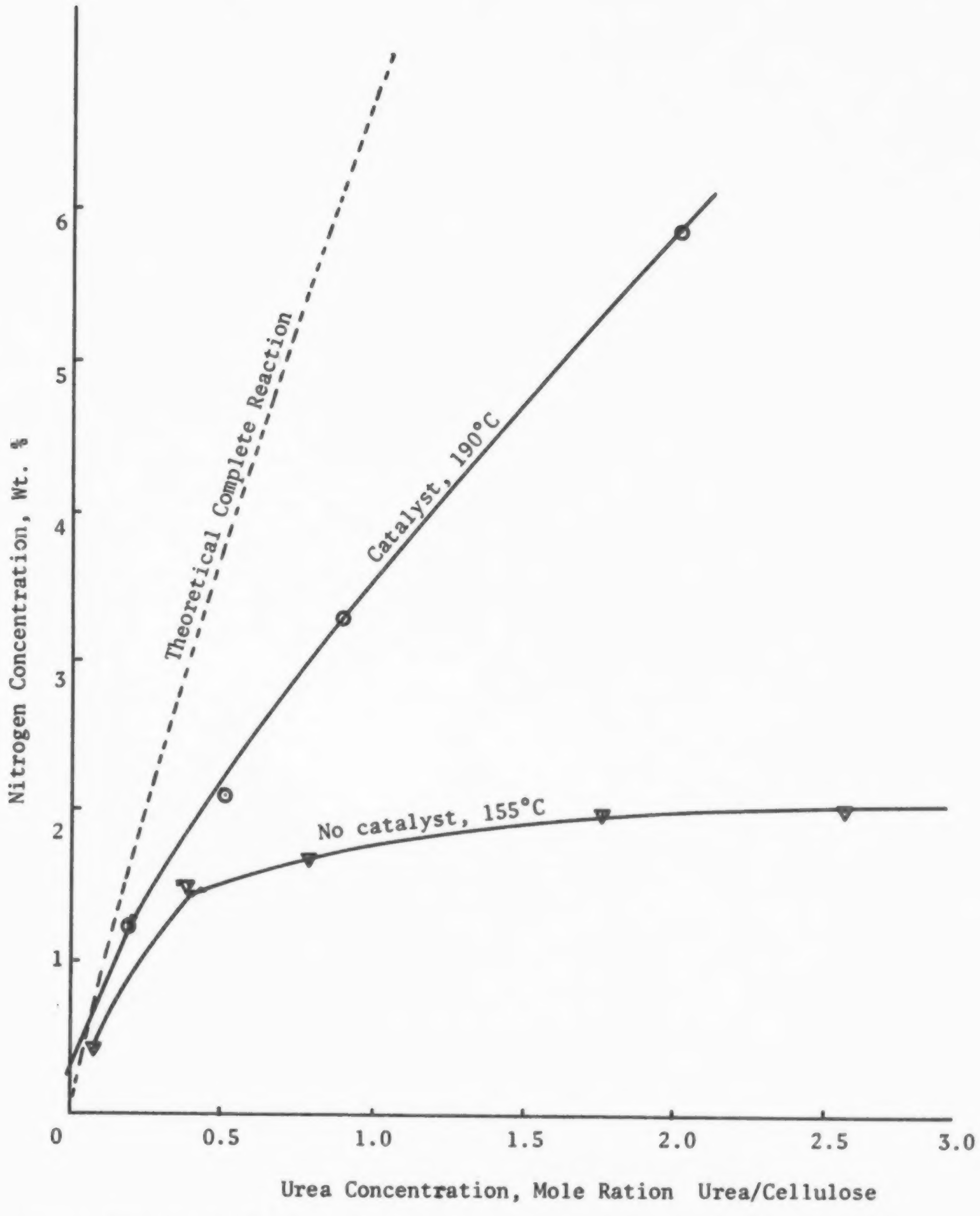


Figure III. C. 4 Effect of Reactant Concentration on Nitrogen Concentration. Time = 1 hr.

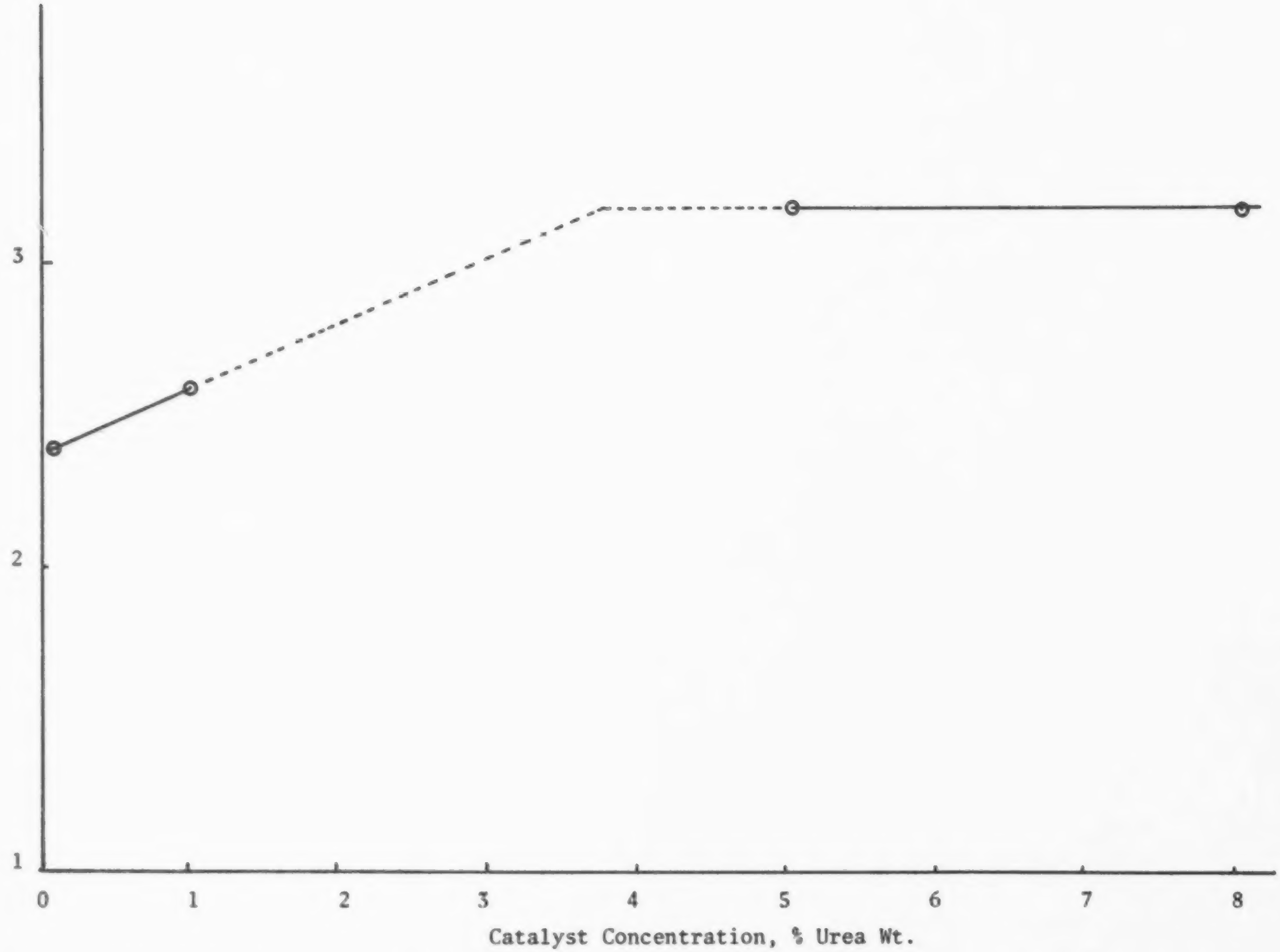


Figure III. C. 5 Effect of Catalyst Concentration on Nitrogen Concentration. (Cupric Chloride)

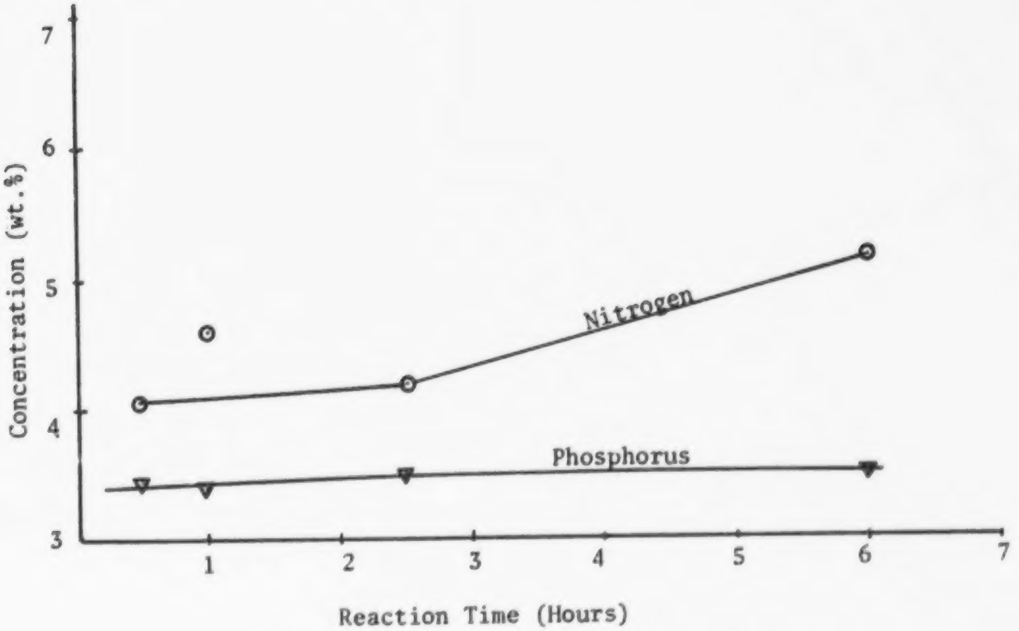


Figure III. C. 6 Effect of Reaction Time on Phosphorus Concentration

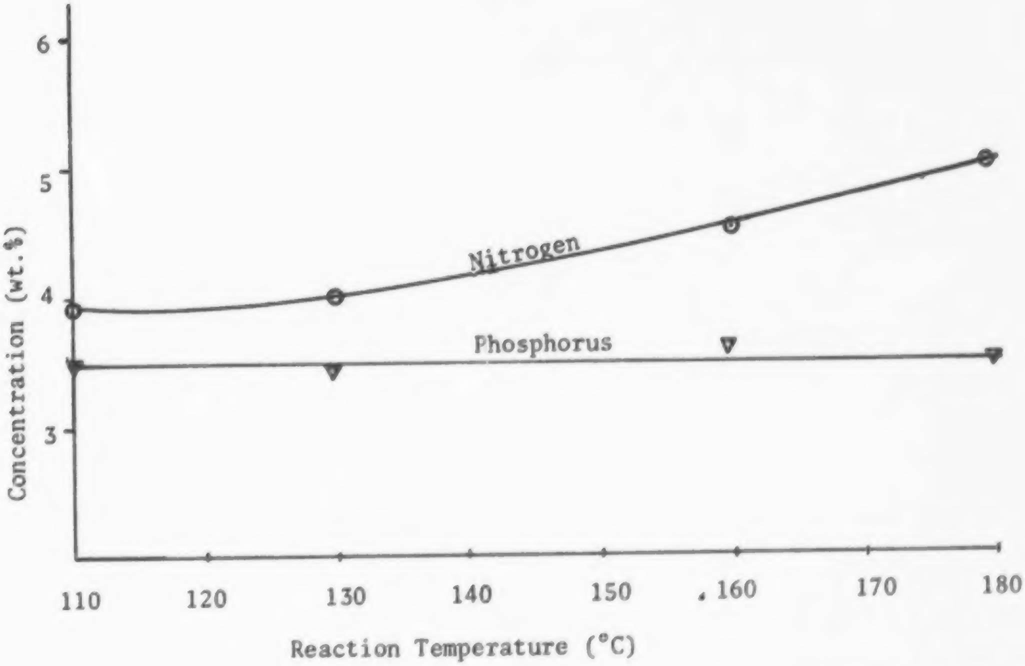


Figure III. C. 7 Effect of Reaction Temperature on Phosphorus Concentration

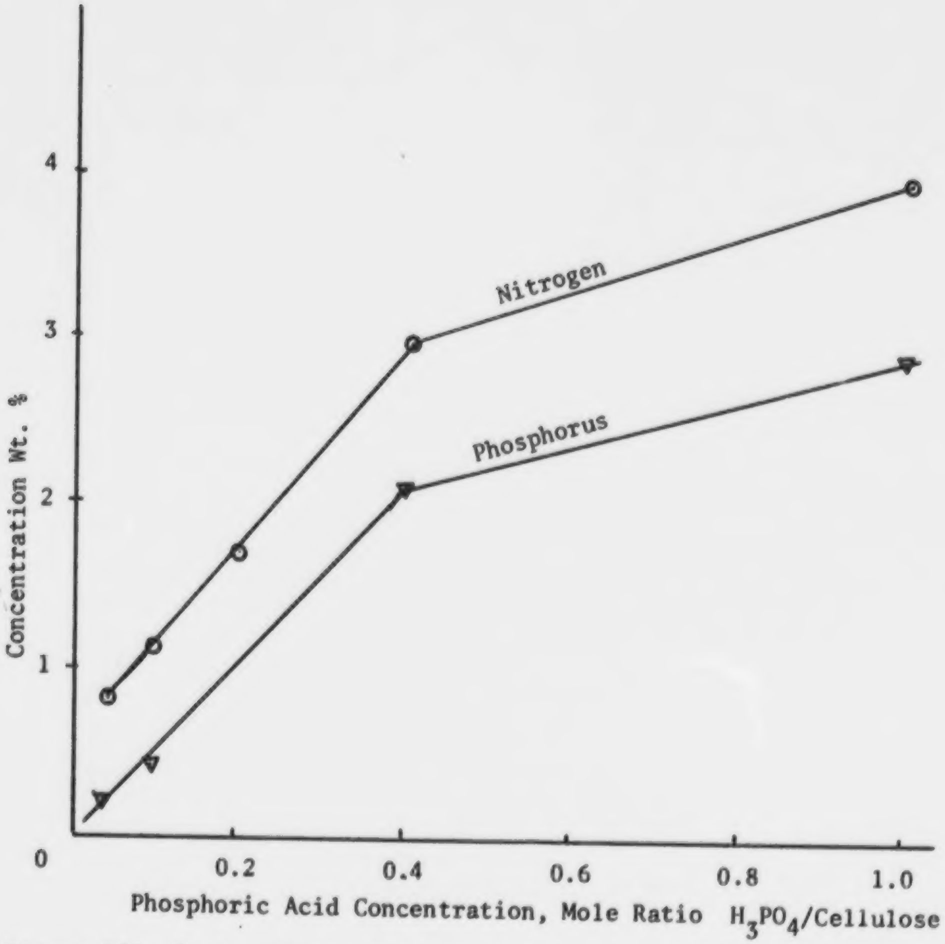


Figure III. C. 8 Effect of Reactant Concentration on Phosphorus Concentration

Table III. C. 1. Soil Test With Amino Cellulose

State				
Reaction Pressure, P.S.I.	132	900	980	2700
Reaction Temperature, °C	23	90	185	300
Reaction Time, min.	900	10	30	60
N Concentration (unwashed), %	0.8	1.7	4.1	11.2
Production, gms.	10.5	17.6	13.5	12.4
N Concentration, (washed), %	0.3	0.9	3.1	10.5
Production, gms.	5.7	7.1	10.2	12.4
Standards				
No Fertilizer -- 9.5 gms., mono ammonium phosphate 31.4 gms.				

Table III. C. 2. Phosphorylation of Straw

Straw weight, grams	20	20	20	20
Phosphoric Acid, grams	15.3	15.2	14.8	14.6
Reaction Temperature, °C	110	110	110	110
Reaction Time, hours	64	64	64	64
Product Weight, grams	26.6	26.6	26.6	26.6
Product Weight (washed), grams		11.7		12.0
Phosphorus Concentration, weight %	20.8	3.1	21.7	3.2

Table III. C. 3. Nitrogen and Phosphorus Enrichment of Straw

Sample	Phosphorus Concentration, Wt. %		Nitrogen Concentration, Wt. %	
	Unwashed	Washed	Unwashed	Washed
1	13.3	3.4	14.5	5.6
2	13.3	4.8	14.3	4.8
3	11.8	2.5	12.8	4.1
4	12.3	3.8	13.9	5.5
5	11.5	2.9	14.9	5.1

Table III. C. 4. Soil Test With N-Enriched Paper

Reaction Time, (hrs)	5	0	1	1	0	1	1	1
Reaction Temperature, (°C)	155	-	155	155	-	145	145	145
Washed, Unwashed (w,u)	w	w	u	w	w	u	u	w
Nitrogen Concentration, (%)	3.8	0.1	10.2	1.6	0	12.2	12.2	1.7
Grass Production. (grams)	10.3	36.6	32.4	43.9	8.9	24.1	32.5	42.4
Standards								
No Fertilizer	8.5	33.2	33.2	33.2	8.5	8.5	14.4	33.2
Commercial Fertilizer	28.1	46.5	46.5	46.5	28.1	28.1	36.3	46.5

Table III. C. 5. Soil Test With N and P Enriched Paper

State	1	2	3	4	5	6	7
Reaction Time, (hrs)	1	4	4	4	0.5	0.5	0.5
Reaction Temperature, (°C)	155	155	155	155	190	190	190
Washed, unwashed, (w,u)	w	u	w	w	u	w	w
Nitrogen Concentration, (%)	7.3	13.1	5.1	5.1	11.4	6.6	6.6
Phosphorus Concentration, (%)	4.6	11.7	8.7	8.7	8.8	6.4	6.4
Grass Production, (grams)	35.3	31.5	63.4	27.8	37.1	32.7	27.4
Standards							
No Fertilizer	14.4	6.5	6.5	11.5	14.4	14.4	8.5
Commercial Fertilizer	36.3	31.5	31.5	31.0	36.3	36.3	28.1

Acetylation of Wastes

The first recorded acetylation of cellulose has been credited to Schutzenberger (4:61) in 1865. However, the sulfuric acid catalyst used reacted with the cellulose to form sulfate esters. These groups cause the product to be unstable. Later it was found that by using a hydrolysis step, the acetate could be converted to a more useful form.

A typical reaction scheme for the commercial production of cellulose acetate can be shown as

cellulose

acetic acid & catalyst ↓ acetic anhydride

esterification

↓

water in acetic acid

↓

hydrolysis

↓

filtration

↓

wash and stabilize

↓

dewater and dry

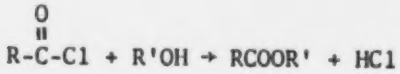
↓

screening and packaging

Chemistry: There are several methods of esterification that can be used to acetylate cellulose in the laboratory. Since cellulose contains hydroxyl (OH) groups, it must be considered to be an alcohol, and will be denoted by the usual symbol ROH. The acid will be noted as $R-\underset{\underset{O}{\|}}{C}-OH$.

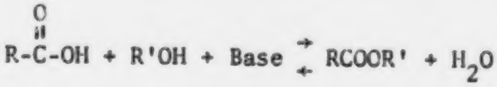
Reactions That Produce Esters In general there are four reactions that can be used to produce an ester. These reactions can be shown as:

1. The reaction of an acid chloride with an alcohol



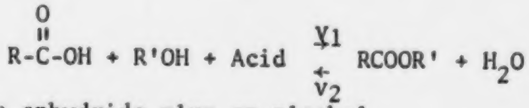
$$R\text{-}\overset{\overset{\displaystyle O}{\parallel}}{C}\text{-}Cl + R'OH \rightarrow RCOOR' + HCl$$

2. An acid plus an alcohol using a basic catalyst



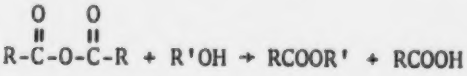
$$R\text{-}\overset{\overset{\displaystyle O}{\parallel}}{C}\text{-}OH + R'OH + \text{Base} \rightleftharpoons RCOOR' + H_2O$$

3. An acid plus an alcohol using an acid catalyst



$$R\text{-}\overset{\overset{\displaystyle O}{\parallel}}{C}\text{-}OH + R'OH + \text{Acid} \overset{v_1}{\underset{v_2}{\rightleftharpoons}} RCOOR' + H_2O$$

4. An anhydride plus an alcohol



$$R\text{-}\overset{\overset{\displaystyle O}{\parallel}}{C}\text{-}O\text{-}\overset{\overset{\displaystyle O}{\parallel}}{C}\text{-}R + R'OH \rightarrow RCOOR' + RCOOH$$

Reaction three is usually used commercially to produce cellulose acetate. As shown, the reaction is reversible, and the velocity (v) of each reaction depends on the rate constant and the concentration of the reactants and products.

$$v_1 = k_1 \text{ (RCOOH) (R'OH)}$$

$$v_2 = k_2 \text{ (RCOOR') } (H_2O)$$

It is easily seen that by using an excess of acetic anhydride to remove the water, the reaction will be forced toward the formation of the ester RCOOR'.

It has been found that when using sulfuric acid catalyst, 5% by weight of the cellulose, a very rapid reaction takes place at the beginning of the esterification producing sulfate esters. Because of the large concentration of acetic acid, a transesterification occurs replacing the sulfate groups with acetyl groups. Some sulfate groups remain even after long reaction times. A hydrolysis step is employed to remove the sulfate groups. Acetic acid, containing enough water to make the final solution to about 0.5% water, is added to the reaction mixture. This water not only hydrolyzes the sulfate groups but destroys the excess anhydride as well. This hydrolysis step should be fairly short, i.e., about 5 hours or less because it has been found (2) that long hydrolysis times reduce the acetyl content and again increase the sulfate content.

The usual laboratory procedure for preparing cellulose acetate for esterification would be to soak the cellulose in water and replace the absorbed water with glacial acetic acid. This requires large quantities of water and acid, and has been replaced in industry by simply soaking the cellulose with acetic acid for 1-2 hours before acetylation takes place.

Several publications have reported the preswelling of the cellulose with various materials to insure a more complete reaction. A fairly recent paper by Klenkova et. al. (1) reported the preparation of cellulose triacetate with high degrees of polymerization (1100-1150). They used methylamine or ethylenediamine to preswell the cellulose. The amines were subsequently removed with organic solvents then with acetic acid. It is doubtful that this complicated process will be used by industry.

Malm et. al. (3) studied the far hydrolysed cellulose acetates, i.e., cellulose acetate with a large portion of the acetyl groups removed by hydrolysis. They found the products to be soluble over a wide range of acetyl content if they varied the water to acetone ratio in the solvent. For example a 1:1 mixture of water and acetone (they did not state whether this was mole %, weight %, or volume %) was capable of dissolving cellulose acetates with an acetyl content from about 16 to 35%.

Catalysts Used In Esterifications

Numerous acids and acid salts have been used in the laboratory to produce cellulose acetate. Typically one finds zinc chloride, perchloric acid, sulfonic acids, various halogen acids, and sulfuric acid being used as catalysts. Commercially sulfuric acid is used because of its reasonable cost and lack of corrosion of the equipment used. Its use does require the hydrolysis step however.

Basic catalysts are usually limited to pyridine or basic salts such as sodium acetate.

Recovery Of Excess Reagents

Stannett (5:40) tells us that solvent extraction, followed by solvent distillation, is used to reclaim the dilute acetic acid produced by the precipitation step of the acetylation process. She suggests the use of ethyl acetate as a solvent because ethyl acetate removes excess water as an azeotropic mixture. The ethyl acetate is next to distill, and finally the acetic acid is removed at the bottom of the column.

There are several alternate solvents that could conceivably be used, but will not be listed here.

Process: Acetylation has been conducted on a laboratory scale using the vapor phase, fiber, and solution processes.

Vapor Phase

A schematic diagram of the vapor phase process is shown in Figure III. D. 1. The cellulosic waste is placed in an oven and hot air containing acetic anhydride vapors is circulated through the oven. Since acetic acid is formed by the reaction, it can be condensed from the exit gases. A catalyst, such as pyridine, must be used to swell the fibers. Although this acetylation process does not produce a high degree of acetylation, it does improve dimensional stability in paper and wood, and in laboratory tests it has produced adequate acetylation in ground paper to form a solid disc on pressing.

Solid waste moisture content and nature of the solid waste will be important in this process since the anhydride reacts with water to form acetic acid and since the anhydride is being transported in the air. The waste should be dried and ground because reduction in particle size will increase the surface area and promote faster and more complete acetylation.

Catalyst selection is important in rate of reaction, cost, and recovery. Pyridine is not the only catalyst that has been used in this process, but it does have some advantages, in particular it is easily volatilized, and it readily expands the cellulose fibers. The catalyst concentration will undoubtedly have some effect on the availability of cellulose hydroxyl groups for reaction.

Reaction temperatures must be controlled to maintain the greatest yield at the least cost. If the reaction temperature is set below the boiling point of acetic anhydride (~140°C), then the condensation of anhydride on the cellulose will facilitate the reaction; however, if the temperature is above the boiling point of acetic acid, (~118°C), then the acid formed will immediately be vaporized. Since the boiling point of pyridine is about 115°C, it will remain in the vapor state at these conditions. Reaction temperatures above 140°C would insure that the anhydride remained in the vapor state. In a batch reaction, the temperature could be maintained above 140°C after the reaction to remove the excess anhydride.

The reaction time will determine the degree of acetylation until the reaction is complete. The rate at which anhydride and catalyst is carried to the oven will be determined by the air flow and air temperature. The acetylation rate will be influenced by the oven temperature and the availability of the cellulose hydroxyls. Sufficient reaction time will be needed to produce an acetyl content that will allow the cellulose to have thermoplastic properties.

The Fiber Process is schematically shown in Figure III. D. 2. The dry cellulosic waste is reacted with a solution containing acetic anhydride, a catalyst, and a solvent. Acetic acid and cellulose acetate are produced by the reaction. The reaction solution is separated from the acetylated waste solids. The solvent and catalyst are reclaimed for reuse, leaving the acetic acid as a by-product. The acetylated waste is then washed and dried. This process can be used to prepare the triacetate by repeated acetylations of the product.

The solid waste must be dry. Although the particle size is not as important as in the vapor phase process, a reduction in particle size may facilitate waste handling. The anhydride is carried to the cellulose by the solvent, but the product does not dissolve in the acetylation solution.

Perchloric acid serves as a good catalyst for this process since it does not combine with the cellulose, however it can be a hazard under some conditions. Catalyst concentration will influence the rate of the reaction.

Several organic solvents have been evaluated for this process including toluene, methylene chloride, and ethylene chloride. The solvent prevents the cellulose acetate from dissolving and carries the acetic acid away. The solvent can be reclaimed for reuse by removing the acetic acid. The degree of acetylation will be determined primarily by the concentration of acetic anhydride used in the acetylating solution.

This reaction will proceed at room temperature but normally a temperature of about 50°C is employed. Since the reaction is exothermic, the reaction temperature rises during the reaction and often reaches 50°C without the addition of heat. The reaction proceeds rapidly and a complete reaction is usually achieved in less than 10 minutes.

After the reaction is complete, the acetylating solution can be separated from the cellulose acetate by filtration or by centrifuging. Since some solvent remains in the cellulose acetate, an alcohol wash is used instead of water. Ether can be used to remove the alcohol or it can be evaporated. The resulting cellulose acetate is normally dried at 60°C.

Solution Process A schematic diagram of the solution process is shown in Figure III. D. 3. The solid waste is reacted with a solution containing acetic anhydride, acetic acid, and a catalyst, usually sulfuric acid. The cellulose acetate produced dissolves in the acetylating solution. Any solids left in the mixture can be removed by filtration. The cellulose acetate is precipitated in water, and if it is passed through tiny holes, it will form threads of the cellulose acetate polymer. The solid is separated by filtration and any combined sulfate is neutralized by addition of sodium carbonate. After further washing, the acetate is dried.

The solid waste composition is least important in this process, since the acetate produced goes into solution. Of the three processes, impurities which influence the reaction will have the most effect in this one, however inert solids can be removed by centrifugation or filtration.

The catalyst used in the laboratory was perchloric acid although sulfuric acid is normally used. The catalyst concentration will affect the nature of the product, since the sulfuric acid is a combining catalyst and until hydrolyzed the product is actually a mixed ester.

Experimental results: Cellulose acetate has been prepared in the laboratory from samples of commercial refuse, paper, and straw. Three acetylation processes have been used; vapor phase, fiber, and solution.

Vapor Phase Process Two samples of paper were acetylated using the vapor phase process. Hot dry air (120°C) was passed through acetic anhydride to pick up vapors then was passed through a flask containing the paper. The catalyst, pyridine, was dissolved in the anhydride. The reaction was allowed to continue for 2 hours at 120°C and then the excess anhydride was driven off at 150°C for 12 hours. After washing and drying the paper was compressed with 2,000 p.s.i. at 350°F to form a plastic disc.

The weight gain for each of the two samples was 22% and 31%, respectively, approximately equal to that expected for formation of the monoacetate (26%).

Fiber Process A study of the effect of variables on the degree of acetylation in the fiber process conducted using various samples of cellulosic wastes. The results of these tests are reported below.

Cellulose swelling with water or other chemicals speeds the reaction. Presumably, when the cellulose is "activated", or swollen, prior to reaction with the acetic anhydride, the internal cellulose hydroxyls are made available to the anhydride. The effect of swelling the fibers on the extent of acetylation was determined using 2 samples of filter paper.

One sample was soaked in water and the water was then replaced by acetic acid prior to reaction with the anhydride. The other sample was dried at 110°C prior to reaction. Both samples were acetylated using perchloric acid as the catalyst. The activated sample resulted in a gain in weight of 56% while the non-activated sample resulted in a gain in weight of 55%. Both products were soluble in a 90:10 wt./wt. dichloromethane/methanol solution. A 52% increase in weight would be equivalent to the formation of cellulose diacetate. Under these reaction conditions, soaking the cellulose did not affect the degree of acetylation achieved.

In a similar test, using toluene as the solvent, a different result was obtained. When no acetic acid was present in the toluene and the paper was not preswollen, cellulose acetate with only 12% acetyl content was produced after 20 minutes reaction time, compared to an acetyl content of 23% when DCM was used as the solvent.

When acetic acid was added to the toluene a cellulose acetate with 28% acetyl was obtained after only 2 minutes reaction time.

When the cellulose was preswollen with water and the water replaced with acetic acid, the reaction in toluene produced an acetate with 35% acetyl, while the reaction in DCM produced an acetate with 30% acetyl.

From this evaluation it appears that "activating" the cellulose does have an influence on the degree of acetylation achieved; however, the effect is different for different solvent systems. In addition, the presence of acetic acid in the solvent influences the degree of acetylation, although this effect is also different for different solvent systems.

Reaction time influences the degree of acetylation as shown in Figure III. D. 4. This evaluation was conducted with a sample of commercial paper waste obtained from a Seattle bank. The waste was dewatered with acetic acid and reacted with a solution containing toluene, perchloric acid, and acetic anhydride. After the reaction was complete, the solid acetate was separated by centrifuging. Ethanol was used to remove the toluene and the cellulose acetate was washed in water and dried. Under the conditions of this test, changes in the reaction time did not affect the degree of acetylation.

A second evaluation was conducted to determine the effect of changes in time from 1 to 10 minutes. The results of this test are shown in Figure III. D. 5. Although the degree of acetylation increases with increasing time, a plateau occurred at about 5 minutes reaction time. This plateau corresponds to a degree of substitution of about 1.5 - 1.8. It appears that the introduction of the third acetyl group is somewhat more difficult than the first two.

Anhydride concentration affects the degree of acetylation as shown in Figure III. D. 6. This evaluation was conducted with a sample of commercial paper waste obtained from a Seattle bank. The waste was dewatered with acetic acid and reacted with a solution of toluene, perchloric acid, and acetic anhydride. After the reaction was complete, the solid cellulose acetate was separated by centrifuging. Ethanol was used to remove the toluene and the cellulose acetate was washed with water and dried. An increase in the anhydride concentration resulted in an increase in the degree of acetylation but only 50-70% of the anhydride reacted.

A second evaluation conducted with newspaper confirmed these results. Based on these findings, an anhydride concentration of 2 moles anhydride/mole cellulose would be required to produce the monoacetate, which is the level required in order to impart a thermoplastic property into the product; however, cellulose acetate with 20% acetyl can be prepared withouth any anhydride. Two reactions conducted with acetic acid only, for 1 minute and 14 hours respectively, resulted in products with acetyl concentrations of 13% and 20% respectively, however the physical properties of these products were not determined.

A reaction temperature increase will increase the degree of acetylation. An evaluation of this effect was conducted using a sample of commercial paper waste obtained from a Vancouver brewery. It was dewatered with acetic acid and reacted for 5 minutes with a solution containing 150 ml toluene, 15 ml acetic anhydride, and 0.15 ml perchloric acid. Cellulose acetate samples with 41.6% and 39.0% acetyl respectively were produced.

Catalyst concentration will influence the degree of acetylation as seen in Figure III. D. 7. These reactions were carried out using a sample of commercial paper waste from a Vancouver, Washington brewery. The water was replaced with acetic acid and the reaction was conducted with a solution of toluene, acetic anhydride, and perchloric acid for 15 minutes at 25°C. The acetic anhydride concentration was 3.71 moles anhydride/mole cellulose. The acetyl concentration is reduced when the catalyst concentration is reduced below 1% of the acetic anhydride weight.

The product that was obtained with the use of DCM as solvent exhibits extremely good flow properties in the plastic state. This flow property is not exhibited by acetate made with toluene or made by the solution process, however, removal of the DCM is a problem.

Solvents used in conjunction with the acetylation reaction have a pronounced affect on the results. Since toluene prevents dissolution of the cellulose acetate, it is a solvent only in that it holds the anhydride and catalyst in solution. Because the cellulose does not dissolve in the reaction mixture, the acetate can easily be recovered from the reaction mixture by filtration or centrifugation. The solvent mixture can then be recycled or subjected to a reclamation process. The solids from this process need less water for washing because methanol, which is at least in part reclaimable, is used to remove the residual toluene and acids.

Following separation, the reaction mixture can be distilled and the distillate returned to the system as a starting material for further acetylations. The first portion of the distillate contains an acetic acid-toluene azeotrope, boiling at 104°C. As the toluene is depleted, the temperature of the distillate increases and there is more anhydride present. When the acetic acid has completely distilled, acetic anhydride can be recovered.

The methanol used for the wash is more difficult to reclaim. Traces of acetic acid and acetic anhydride washed from the acetate react with the methanol to form methyl acetate. When this mixture is distilled, the first portion contains methanol, methyl acetate and toluene, then as the toluene is exhausted, the methanol-methyl acetate azeotrope distills. Finally, as the methyl acetate is exhausted, the pure methanol can be reclaimed by distillation. The methanol-methyl acetate azeotrope could be converted to methyl acetate, which would have utilization as a solvent for introducing the plasticizers into the cellulose acetate.

When dichloromethane (DCM) is used instead of toluene, the reaction mixture becomes very gummy and is not filterable, however the solid can be separated by centrifuging.

The waste source has a strong influence on the maximum acetyl concentration obtainable. Filter paper, produces a white powder with up to 44% acetyl content. This material can be formulated and calandered into transparent sheets. As the impurities in the starting material are increased, the product loses its transparency and becomes darker in color.

Newspaper, which contains some lignins produces a light brown cellulose acetate with 42% acetyl content, while municipal refuse produces a dark brown cellulose acetate with 36% acetyl content. This latter sample of municipal refuse was obtained from the Black-Clawson Company in Ohio, and still contained small pieces of inorganic residue although most of the metal and glass had been removed.

Solution Process

Cellulose acetate was prepared from paper and straw using the solution process, but an extensive evaluation of this process was not undertaken since the vapor phase and fiber processes appear to be better suited for chemical treatment of waste cellulose to produce cellulose acetate.

Straw, when acetylated gives a product which is dark brown, brittle, and contains straw components that are not dissolved.

Paper was used in a series of tests to evaluate the effect of changes in catalyst concentration on the degree of acetylation when using samples of newspaper as the source of cellulose. The amount of catalyst, perchloric acid, was varied from 0.16% to 5% by volume, based on the volume of acetic anhydride used. One series of samples was prepared at a reaction time of 1 minute while another series was prepared at a reaction time of 30 minutes.

Perchloric acid, while somewhat more hazardous to use than sulfuric acid, was chosen as the catalyst because it eliminated the need for hydrolysis between the acetylation and the precipitation steps in the solution reactions. Perchloric acid does not form esters with the cellulose as sulfuric acid does. The sulfate esters not only lower the degree of acetylation of the final product, but because of their acid nature, these esters cause hydrolysis of the acetate esters when exposed to atmospheric moisture.

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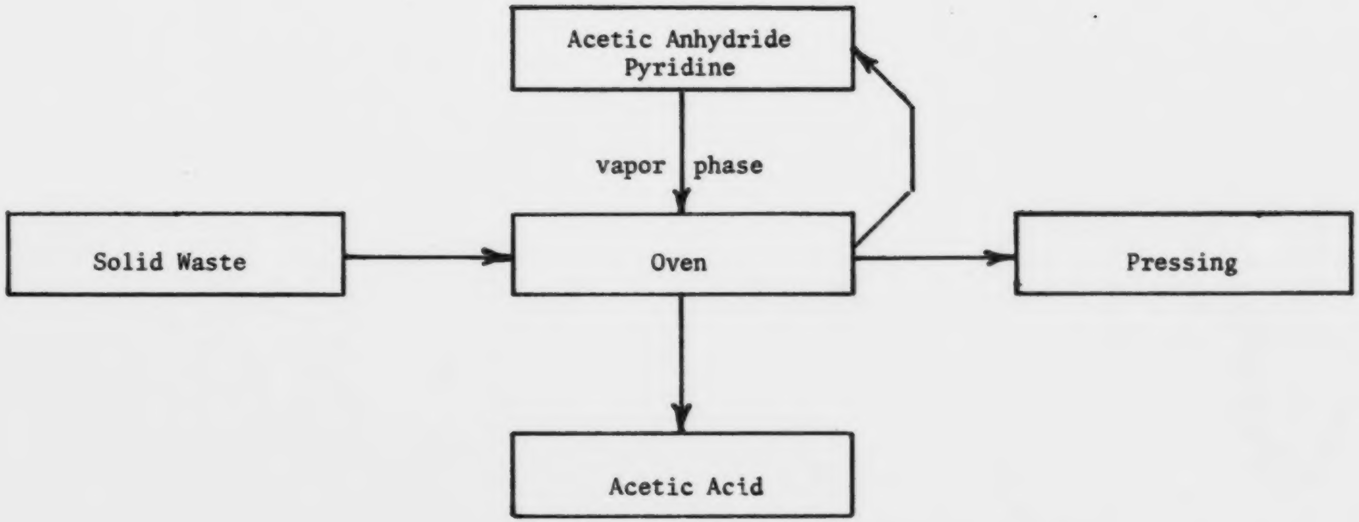

Acetic Anhydride
Pyridine
vapor phase
Solid Waste
Oven
Pressing
Acetic Acid

Figure III. D. 1. Schematic of Vapor Phase Acetylation of Solid Waste.

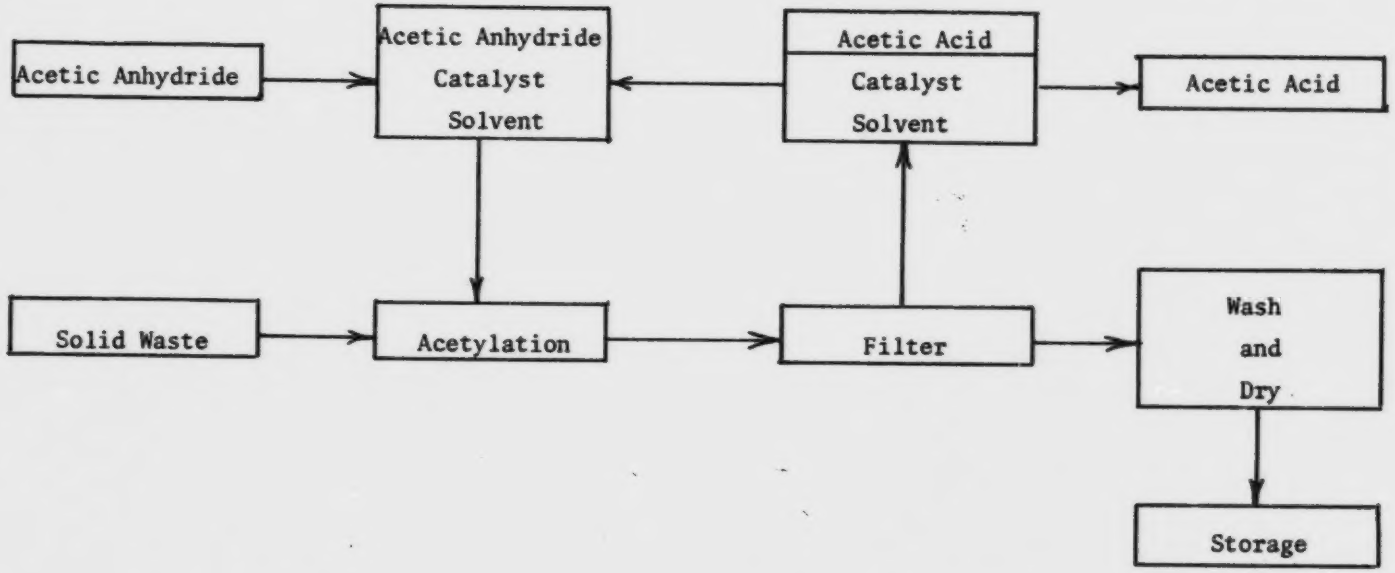

Acetic Anhydride
Acetic Anhydride
Catalyst
Solvent
Acetic Acid
Catalyst
Solvent
Acetic Acid
Solid Waste
Acetylation
Filter
Wash
and
Dry
Storage

Figure III. D. 2. Schematic Diagram of The Fiber Process of Acetylation of Solid Wastes.

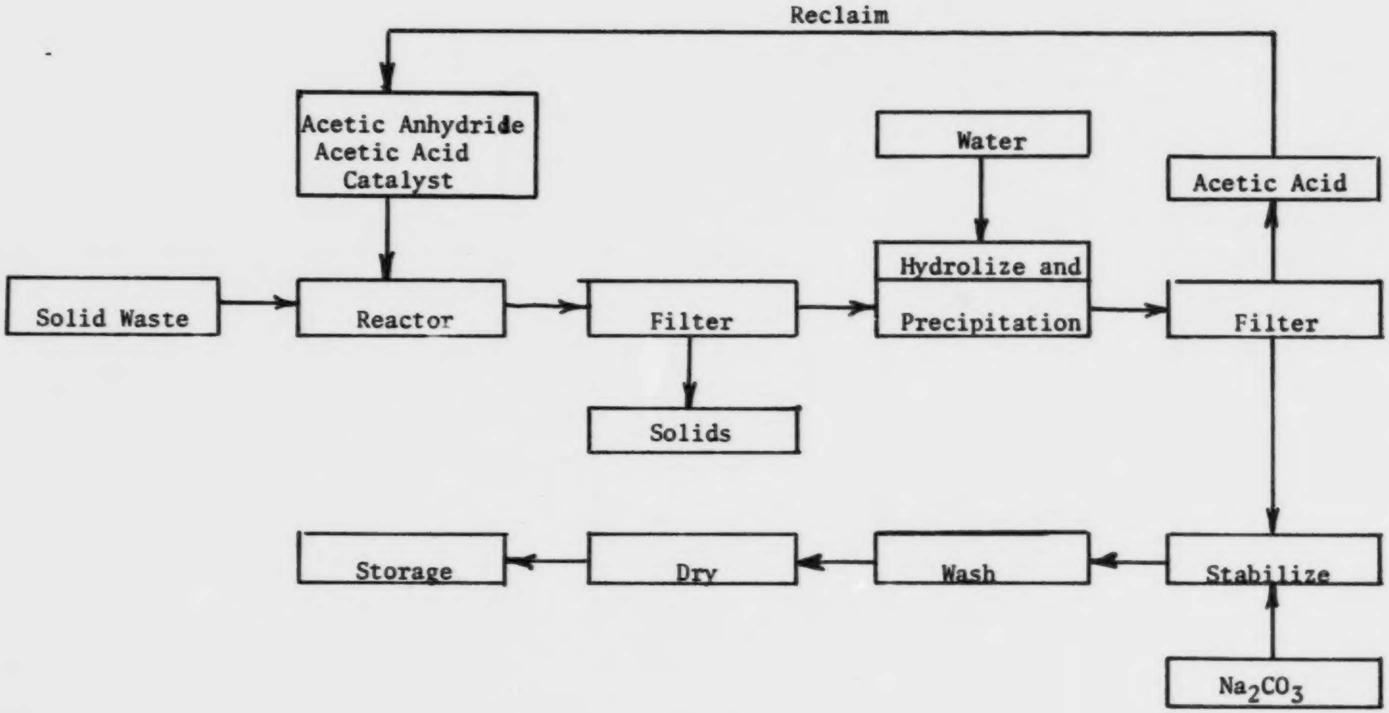

Reclaim
Acetic Anhydride
Acetic Acid
Catalyst
Solid Waste
Reactor
Filter
Solids
Water
Hydrolize and
Precipitation
Acetic Acid
Filter
Stabilize
Na_2CO_3
Wash
Dry
Storage

Figure III. D. 3.' Schematic Diagram of The Solution Process for Acetylation of Solid Waste.

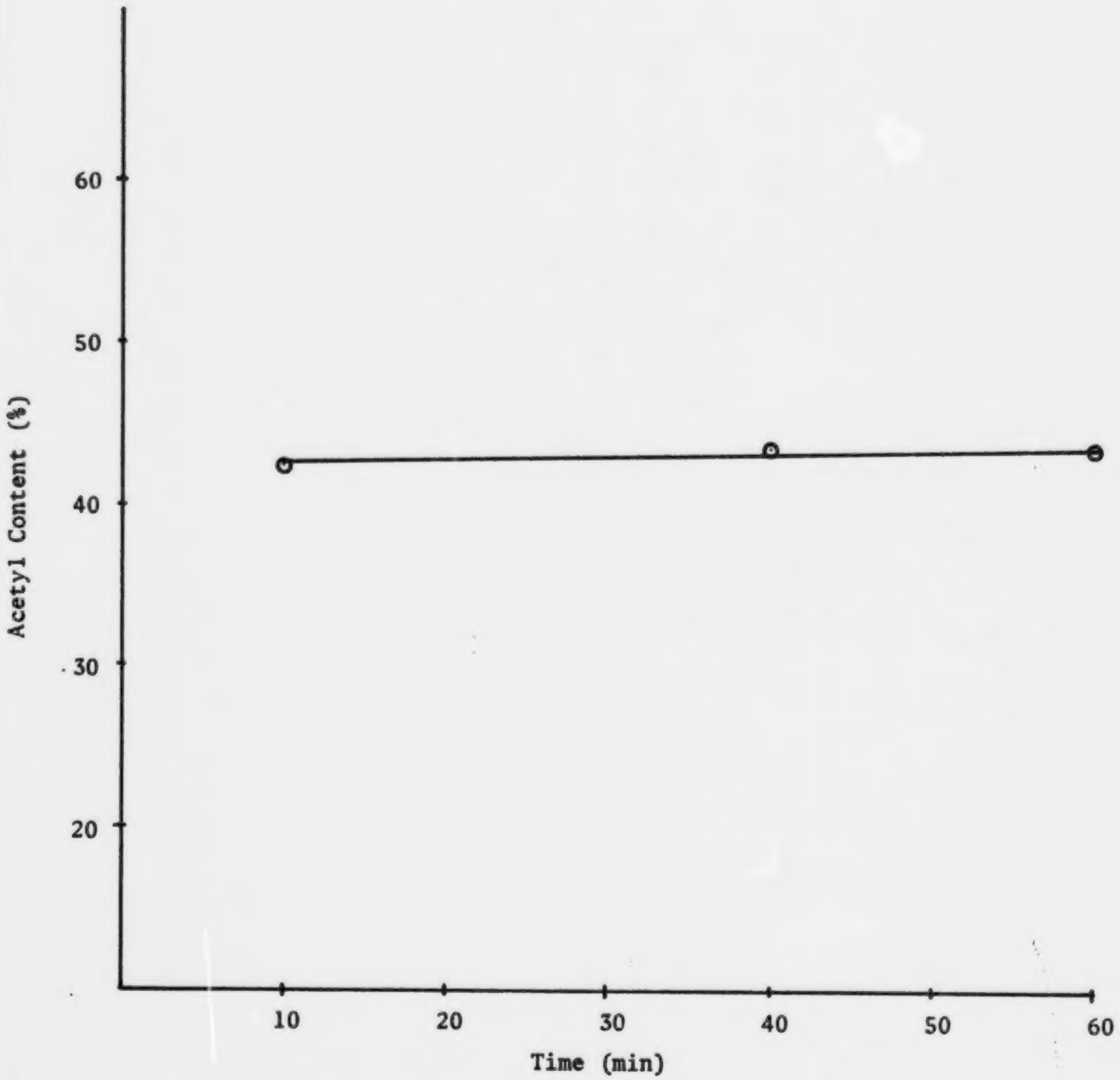


Figure III. D. 4. Effect of Reaction Time on the Degree of Acetylation.

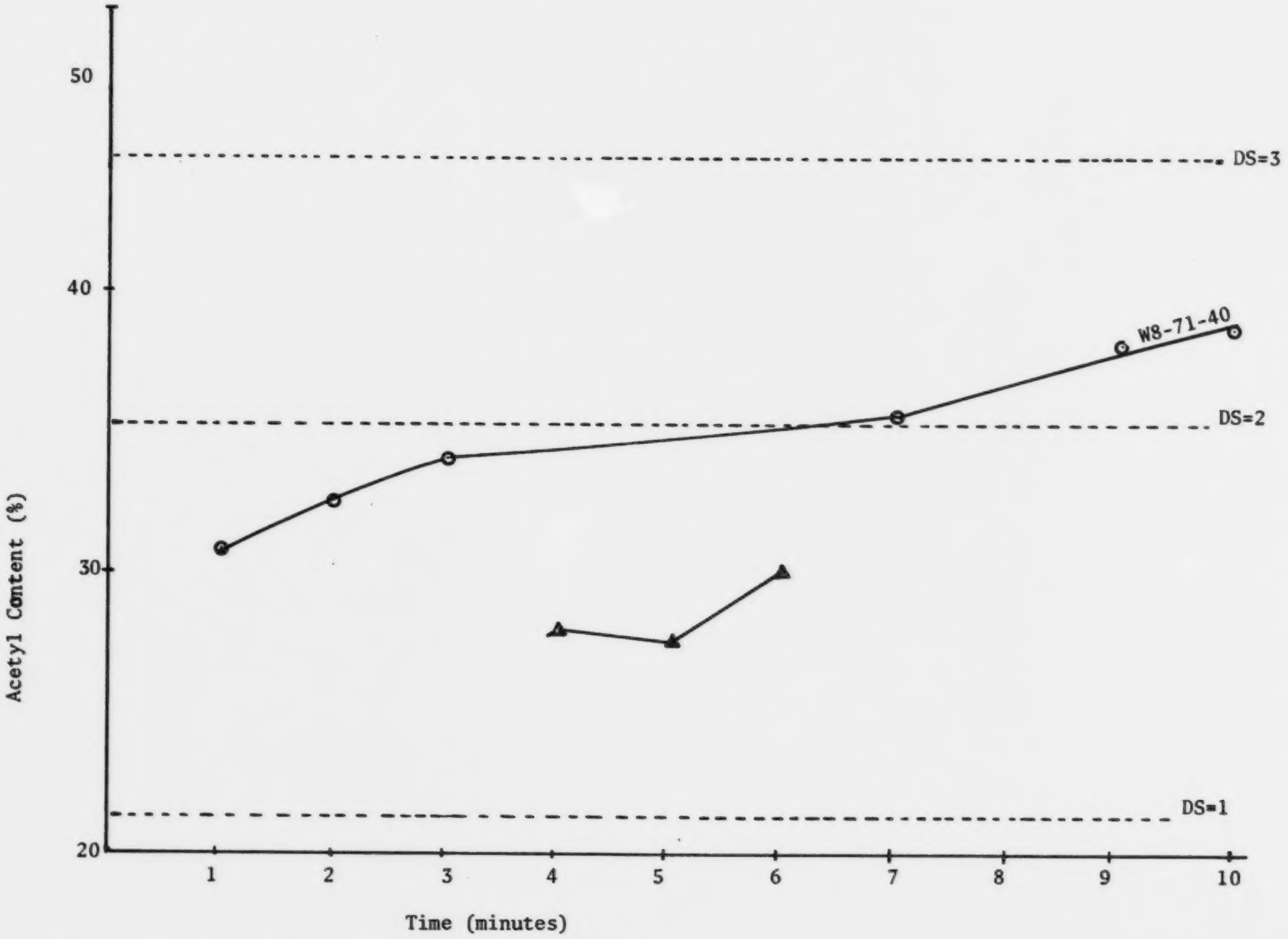


Figure III. D. 5 Effect of Reaction Time, from 1 to 10 Minutes, on Degree of Acetylation.

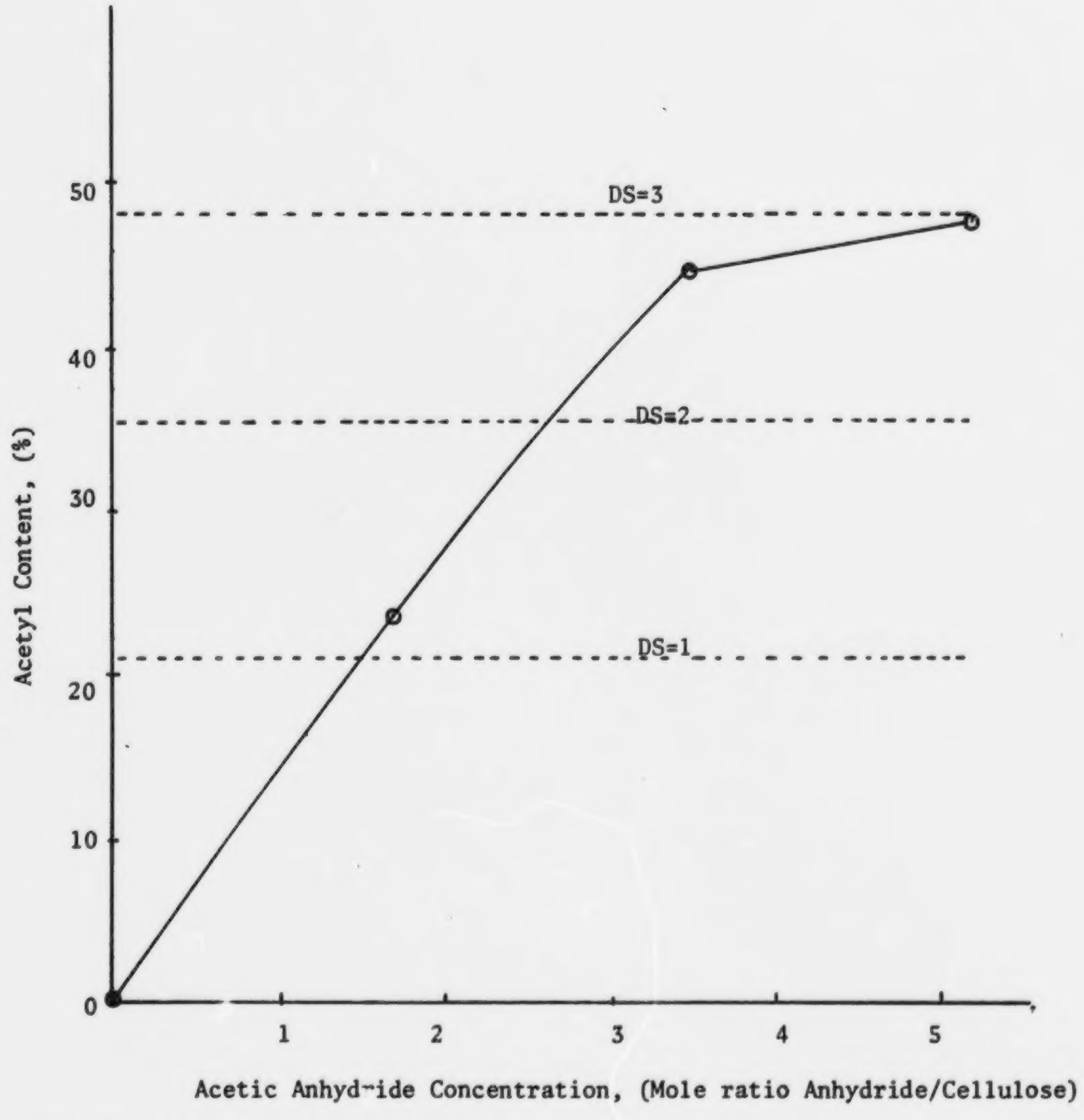


Figure III. D. 6 Effect of Anhydride Concentration on Acetyl Content.

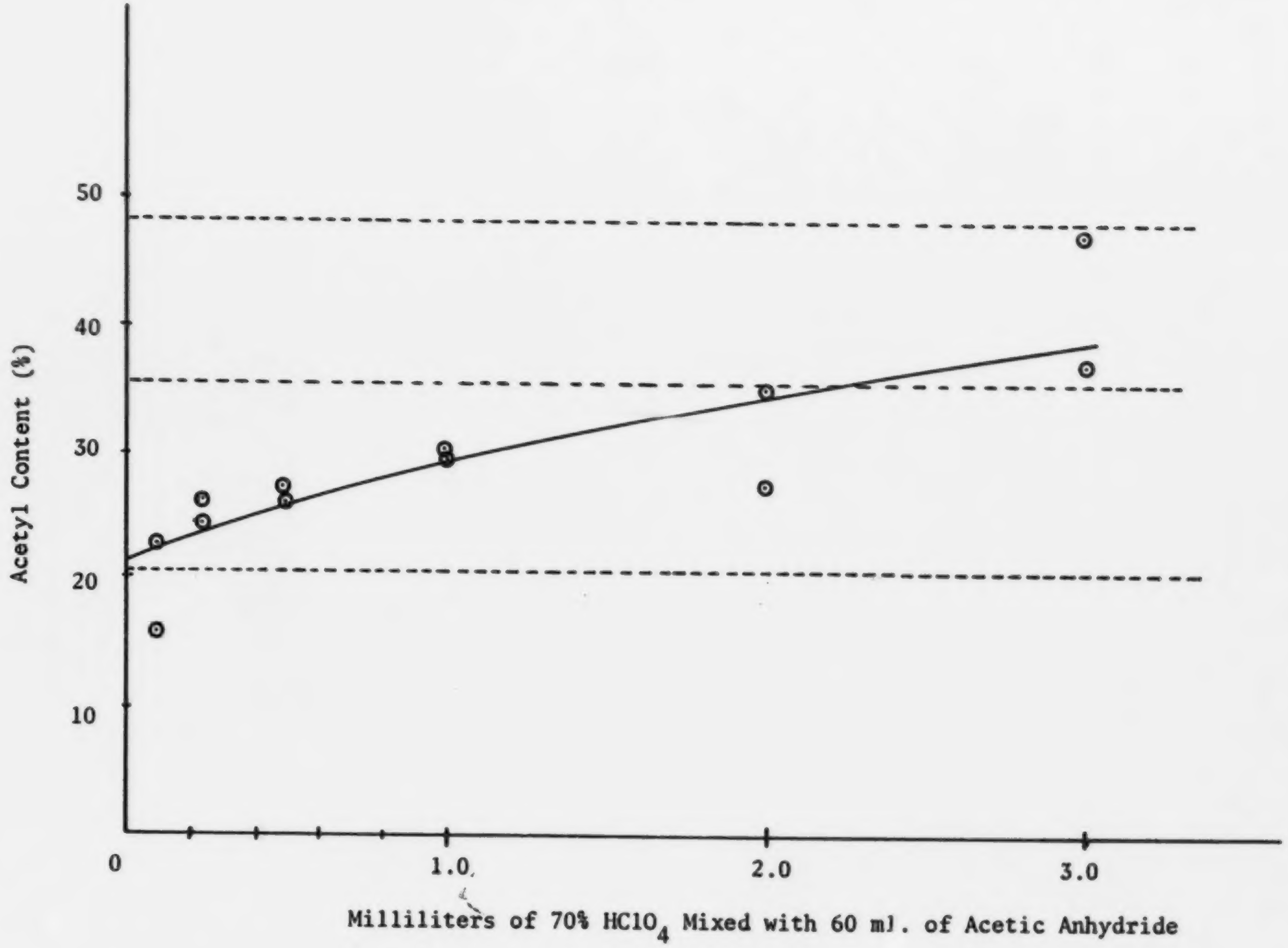


Figure III. D. 7. Showing the Relationship Between Catalyst and Degree of Acetylation When Using Perchloric Acid, with a Reaction Time of One Minute.

Hydrogenation of Wastes

"Future Fuels; Where From" was the title of an article (30) describing one of the problems facing this nation. It is felt that this problem can be partially solved along with the problem of the refuse crisis, by converting the wastes to gas and oil through hydrogenation. Liquid fuels are easier to transport and presumably have a higher energy value than the solid fuels.

In 1966 a preliminary literature search concerning the problem of our fuel shortage was undertaken. It was found that Glover (38) and Linsly (62) both reported that the use of gas and oil was outstripping the development of new reserves. They stated that this condition had existed since 1958. By 1970 the news media had taken up the hue and cry about the energy crisis (34, 84). Even the oil journals were admitting that the demand was increasing so rapidly that by 1990 the world demand for oil would be 100 million barrels per day (90).

By 1967 some people were beginning to look toward controlled nuclear reactors as a source of electric power which would relieve some of the strain on the gas, oil, and coal reserves (86, 87). Other are convinced that conversion of coal to oil and gas is the answer to the energy shortage (27, 28, 29, 70). A relatively new concept is the atomic "mining" of a gas and oil from oil shale and oil sands. (69, 71). Thermal processing of shale and sand is being examined in attempt to bolster our sagging reserves (31).

In the past 5 years there has been no reported gain in the reserves to production ratio for either gas or oil. In fact the reserves to production ratio is still reported to be declining (40).

Chemistry: Man in his search for an understanding of the world in which he lives has done much toward finding the answer to how coal and oil could have been formed. In 1913, Heuser (44) found that a coal-like substance was formed in the digester system at a pulp mill. In 1922 Willstatter and Kalb (88) studied the reduction of carbohydrates and lignins by the action of hydriodic acid and red phosphorus. In 1923, Fischer and Tropsch found that iron acting as a catalyst would produce hydrocarbons from carbon monoxide and hydrogen (80).

Berl and his co-workers published several papers on the formation of a coal-like substance from cellulosic compounds, and the conversion of this "coal" and carbohydrates to oil (10, 11, 12, 13, 14, 15, 16, 17, and 18). They reported that the most positive results toward coal formation resulted when the material was treated under pressure in an alkaline medium (13). The "protoproduct" was subsequently treated with "ferrum reductum" and iodine under 100 atmospheres of hydrogen (16, 17) to produce an oil. In another article Berl (15) postulated the formation of aromatics and polycyclic aromatics from carbohydrate molecules. Other references to Berl and his co-workers would have to include the journals *Papier-Fabrikant* (18:141-149) and *Zeitschrift fur Physikalische Chemie* (14:71-93).

About 1935 there was a flurry of work reported by Boomer et al. (21, 22, 23, and 24), in which they hydrogenated various substances in tetralin and similar media. It was reported that the "oil" from the treatment of grain screenings was very odorous, acid, contained considerable oxygen and darkened rapidly (24:353).

Kurihari and Yoshioka (59) reported the production of gasoline by hydrogenation of the oil produced from the hydrogenolysis of a mixture of peat and tetralin. Henze, Allen, and Wyatt (43) treated cotton hull fibers with base then hydrogenated the product. They found that 7% base gave the best results. Geerards et al. (37) reported the hydrogenation of carbohydrates.

More recently Ichikawa et al. (49) formed C_1-C_5 hydrocarbons from CO and H_2 by using electron donor-acceptor complex films as catalysts.

Appell, Wender, and Miller of the Bureau of Mines reported the conversion of urban refuse to oil using the water-gas shift to hydrogenate paper (2). They reported a yield of 41% oil. This oil from paper had a relatively high, 20%, content of oxygen (2:4).

Much work has been done in the field of partial hydrogenation of carbohydrates. In most cases the products are polyalcohols although hydroxyketones have been reported by Gurkan (41). Belandin et al. (6, 7) used Ruthenium on a carrier in the presence of mineral acids to produce sorbitol. Van Ling and Vlungter (85) produced polyalcohols, reporting the analysis of these polyols by gas chromatography and paper chromatography. Haidegger et al. (42) produced sorbitol by the reduction of glucose with ammonia synthesis gas.

Kasehagen (55) obtained a patent for the production of glycerol from reducible sugars. A year later Van Ling and Vlungter (85) also reported the formation of glycerol through the hydrogenolysis of saccharides. Bizhanov et al. (19) reported the use of a catalyst, consisting of nickel, aluminum, and iron with about 2% manganese added, to hydrogenate monosaccharides.

Lignin and lignin containing compounds have been hydrogenated by several methods. Besides the earlier mentioned work of Berl and his co-workers we find that Peterson (68) obtained aldehydes, acids, and phenolic compounds from the hydrogenolysis of bark using Raney nickel as the catalyst. Rieche et al. (76) used MnO_3-Fe_2O_3 to hydrogenate lignin. Matsukura and Sukakibara (63), and Ohta and Sukakibara (65) examined the products from the hydrogenolysis of protolignin and reported finding substituted phenylpropane and substituted phenylpropanol. Pepper and Lee (67) have reported a study of catalysts for lignin hydrogenolysis.

Temperature Effects Blackwood, McCarthy, and Cullis (20) published a paper on their study of the carbon-hydrogen reaction with coke and chars. They stated that the reaction of coal with hydrogen was dependant on temperature treatment history and not on the source of the coal. They were primarily interested in gasification rather than liquefaction of the coal.

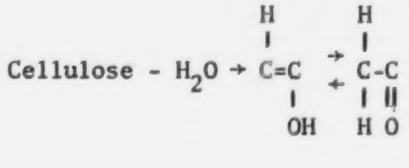
Dehydrogenation was noted by Benson and O'Neal (9:515) while studying the kinetics of the reaction of alkyl iodides with hydrogen iodide. They noted that the alkyl iodides are unstable at elevated temperatures, possibly forming free radicals. Raley et al. (75), Mullineaux and Slaugh (64) and Slaugh et al. (79) conducted a study of high temperature dehydrogenation of hydrocarbons using iodine as a catalyst. They concluded that the reaction probably proceeded through an aliphatic free radical mechanism. Hodgson (45) also studied the reaction of iodine with various organic compounds at high temperatures and found that a dehydrogenation occurs at temperatures above 350°C. Adelson et al. (1) published the kinetic data for reaction rates and the rate constant for the dehydration of isopentane by iodine in the presence of oxygen at 500°C. They postulate 19 steps in the reaction.

Pyrolysis products are similar to many of those found in the hydrogenations referred to earlier in this paper. Many listed products which were very similar to those listed by Hurd (48:270-289) for destructive distillation of cellulosic compounds. Hurd (48:282) lists alcohols, acids, ketones, aldehydes, phenolics, hydrocarbons, gases, water, and charcoal as the products of destructive distillation.

Goos (39:846-850) lists 213 compounds from the destructive distillation of wood, including such items as hydrocarbons, aldehydes, amines, esters, ketones, acids, anhydrides, alcohols, and phenols. Hoffman (47) pyrolyzed municipal refuse at 900, 1200, 1500, and 1700°F. He published values for gas, pyroligneous acids, and char produced, as well as an analysis of the composition of the gas.

Orphey and Jerman (66) studied the liquid condensates from the pyrolysis of municipal refuse reporting aldehydes, ketones, chloroform, acids, water, aromatics, and phenolic compounds. Jerman and Carpenter (53) reported the analysis of the gaseous components from the pyrolysis of solid municipal refuse. They found H_2, O_2, N_2, CH_4, CO CO_2, C_2H_4 and C_2H_6 to be present. They also reported a wide variation in the gas composition from one sample to another, for example the amount of CH_4 reported ranged from 0.2 to 16.14 volume percent.

Arseneau (3) studied the competitive reactions in the thermal decomposition of cellulose and concluded that in the range of 200-280°C depolymerization occurs. He suggests that one reaction of cellulose at elevated temperature might be shown as:



$$\text{Cellulose} - H_2O \rightarrow \overset{H}{\underset{}{C}}=\underset{OH}{C} \rightleftarrows \overset{H}{\underset{H}{C}}-\underset{O}{\underset{\|}{C}}$$

Arseneau's work supported the earlier work of Kilzer and Broido (56).

Catalysts Used In Hydrogenations

Bowen and others, in 1925, reported that the thermal decomposition of cellulosics was not influenced by the presence of hydrogen unless a nickel catalyst was used (25). Fierz-David and Hannig (36) substantiated these findings, but reported that even with nickel catalyst there were aldehydes, ketones, and phenols in the "oil". Bowen and Nash published again in 1926 saying that nickel on alumina was an excellent catalyst. They reported yields of oil up to 45.6 per cent, using nickel oxide catalyst. In their analysis they found 9.21% phenol, 6.41% base, and an oil which, while not identified, was reported to have a "paraffin like" smell.

For many years hydrogenation of coal to form an economical, liquid fuel has been a challenge. Cochran and Sayer (32) in 1959 reported that the results of the work at Billingham indicated this process was not economically realistic. Yet in 1967, *Chemical and Engineering News* (70:96-98) carried an editorial stating that a method for converting coal to gasoline was in the final stage of development. They gave some very interesting economic and engineering figures which indicated that at best the process would be marginal. Laying and Hellwig (60) have reported on the H-Coal process. Coal hydrogasification (8), hydrogenation (58, 54), and fluid bed hydrogenation (89) were all subjects of publications in 1970. Struck et al. (81) studied the kinetics of hydrocracking of coal extract using molten zinc chloride catalyst. Hodgson (46) used a combination of catalysts for the hydroconversion of coal. Lee et al. (61) published on the heat of reaction of hydrogen and coal, Szucs (82) found that iodine promotes the catalysts used in the hydrogenation of coal. Jachh (51) states some of the problems found in the hydrogenation of coal.

Schlinger and Jesse (77), Flinn and Sachsen (35), Bae (4), and Schultz and Linden (78) all have used hydrogen treatment of oil shale for oil recovery.

Quader and Hill (73, 74) have published on their study of the hydrocracking of coal tar, as has Janardanerao et al. (52). An editorial in *Chemical Engineer* (50:50) stated that iodine catalyst improves coal tar hydrogenation.

Experimental Results: A large number of reactions were carried out under varied conditions. The use of different catalysts, various wastes, and two separate gas mixtures was employed.

Catalysts Used In Hydrogenation

Several catalysts and catalyst combinations have been used in the laboratory for the study of the hydrogenation of refuse. Raney nickel, palladium, iodine, hydriodic acid, stannous chloride, tetrahydronaphthalene, and carbon monoxide-water have all been used singly or in combinations to attempt hydrogenation. The greatest yield of hydrocarbon oils was obtained using hydriodic acid.

With Raney nickel, palladium, tetrahydronaphthalene, and the CO-H_2O reactions, sizable quantities of oxygen containing compounds were found to be present in the "oil". These oxygen compounds included groups such as alcohols, ketones, acids, phenols and so on. With hydriodic acid the amount of oxygen containing material was greatly reduced. Some phenols were present, especially in wastes such as bark, straw, etc., which contain lignins.

Recovery of the catalyst from the hydriodic acid runs has been given a cursory examination. In run W6-70-27 about 62% of the HI was recovered in the water layer separated from the oils. Some of the iodine appears to be in the form of organic halides, and some has been found as nearly insoluble material in the solid residue. This latter material may be polymeric in nature with iodine incorporated into the macromolecules.

Materials Treated

A wide spectrum of waste materials have been examined to determine their potential as sources of oil and gas, for fuel, and of petrochemicals. Because municipal refuse is more than half paper, work was started using a fairly pure grade of filter paper, then news print was used for comparison, and finally waste bark and straw were examined.

Waste wood from the timber industry is a problem in the Pacific Northwest, and since much wood is dumped in landfills by the construction industry the feasibility of hydrogenating wood and wood by-products such as bark was examined.

In some seasons large amounts of leaves and grass clippings are hauled to landfills by the collection agencies. Locally there is a problem with grass seed straw being burned; the examination of straw as a source of oil and gas was therefore undertaken.

Rubber tires are becoming a great problem especially since many landfills now refuse to accept these carcasses. Upon treatment under hydrogenation conditions a gas and an oil were obtained. About 50 weight percent of the rubber was found to be inert materials such as carbon black, fillers, metal and so on. It may be possible to return the inert materials to the industry for reuse.

Polyethylene was treated in the high pressure hydrogenation apparatus. Although some of the other wastes contain small amounts of plastic, only polyethylene was specifically treated. The results were not gratifying. At the reaction temperatures used, the only results noticeable were the melting and fusing of the pieces of plastic into one solid mass.

Head Gas Analysis

After a brief examination of the oils from several hydrogenation runs it was decided to examine the head gas in detail first since the gas was less complex. The main components of the gas were carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), hydrogen (H_2) and variable amounts of light hydrocarbons, C_2-C_5, of both olefinic and aliphatic nature. In reporting the information the methane and light hydrocarbons are simply reported as hydrocarbons.

Comparison of the head gas compositions from a series of runs to determine the effects of hydrogen and of catalyst are shown in Table III. E. 1. If one looks at run W6-70-28 using CO and H_2O for hydrogenation, one finds a high CO content in the head gas as would be expected because of the excess CO introduced. The same is true of the hydrogen in the hydrogenation runs.

Since large volumes of gas were used, a collection train was set up, Figure III. E. 1., for the gross examination of the gas and a gas chromatograph was used for the more careful analysis of the component content of gas. However, since hydrogen was used as the carrier gas, and a hydrogen flame detector was on the chromatograph, determination of the hydrogen present in the gas samples was not possible by the gas chromatographic process.

Figure III. E. 1. represents the gas trapping and analysis train. A is the connection to the bomb. B is a base filled bubble scrubbing trap for the trapping of carbon dioxide. Trap C is cooled by a dry ice-acetone refrigerant, while traps D and E are cooled by liquid nitrogen. Point F is a gas sampling port where samples are taken periodically for gas chromatographic or carbon monoxide analysis, Figure III. E. 2. The gas buret, G, indicates the uncollected gas which is primarily hydrogen.

Figure III. E. 2. represents the carbon monoxide analysis train which consists of two traps filled with ammoniacal cuprous chloride solution described by Bach, Dawson, and Smith (5). A 200 milliliter gas tight syringe was used to remove samples from the gas collection train in Figure III. E. 1. point F and transfer the gas for introduction at point F in Figure III. E. 2. The cuprous chloride solution was standardized with known mixtures of gases generated in this laboratory.

Figure III. E. 3. represents the gas chromatographic - mass spectrometric analysis system. The gas chromatograph could be used directly in conjunction with the mass spectrometer or used independently when desired. Samples were removed from the gas trapping system at point F, Figure III. E. 1. by a gas tight syringe and subsequently injected at point F on the chromatograph, Figure III. E. 3.

After the gas from the bomb has been released through the gas train, the valve at A, Figure III. E. 1. is closed and the refrigerants are removed to allow the CO, CH_4 and hydrocarbon gases to be measured and the analysis recorded.

Gas chromatography of the head gas was accomplished using a Varian 1500 gas chromatograph equipped with a 20 foot long, 1/8 inch diameter aluminum column packed with 8% SE-30 silicone rubber on Chromasorb W 60/80 mesh. The oven temperature was maintained at 35°C throughout the sampling of the head gas. Standards were obtained from Matheson Gas Products.

Oil Analysis One of our very early hydrogenations was of the relatively complex material, wheat straw. A sample of the oil was injected onto the gas chromatographic column and the resulting chromatogram revealed 66 peaks. One can quickly see that the oil from these hydrogenations is very complex and difficult to identify.

A less complex material, glucose, was chosen since this is one of the basic units of cellulose. The chromatogram at the oil from hydrogenation of this material gave 59 peaks of which 9 could be considered to be major peaks. This again confirms the complexity of the oil.

A sample of oil from Douglas Fir bark was sent to Standard Oil Company and their results are given in Table III. E. 3. They stated in the cover letter that small amounts of material were distilling at 600°F so that a dry point could not be accurately determined.

When subjected to normal extraction analysis, the oil from the hydrogenation of hospital waste was found to contain primarily hydrocarbons with very small amounts of ketones, aldehydes, and phenols, and trace quantities of acids and amino acids.

Oil from paper contained mostly hydrocarbons, although traces of alkylhalides as well as small amounts of phenolic compounds were detected. Berl et al. (15) postulated that aromatic and phenolic compounds could be formed by the dehydration of glucose type molecules.

Grass straw produced an oil containing alcohols and alkylhalides in small quantities, with the majority of the oil being hydrocarbons. A modified FIA (Fluorescent Indicator Absorption) analysis (33) of the oil from straw indicated the presence of aliphatics, aromatics, and small quantities of olefinic-compounds.

Volume percents were not determined since the apparatus we were using was not of the smaller dimensions indicated by Knight and Groennings (57:1950). The silica gel used was Davidson 923, 100-200 mesh, to meet ASTM standard D 1319-61T, and was purchased from Fisher Scientific Co.

The oil from the CO-H_2O treatment of straw contained considerable amounts of strong acid, amino acids, aldehydes, ketones, alcohols, and phenols. By thin layer chromatography and gas chromatography five of the seven phenolic compounds were tentatively identified as: p-cresol, p-ethyl and p-methyl guaicol, p-ethyl and p-propylphenol. Standards were not available to match the other compounds present.

Oil produced from treatment of straw with hydrogen and tetrahydronaphthalene (THN) contained large quantities of naphthalene and THN. Gas chromatography in conjunction with the mass spectrometer led to the identification of benzene, toluene, cyclohexane, 1-methyl-2-ethylcyclopentane, n-butyl benzene, 1-methyl-2,3-dihydroindene. Several additional compounds have not been definitely identified but most had a peak at mass 31 which is indicative of the presence of a primary alcohol grouping. Upon examining the identified compounds one can see that there is a possibility these all came from rearrangement and breakdown of the THN. It is suggested that any further work with this material should include a treatment of THN without any waste being present.

Table III. E. 2. gives the weight of residue per weight of cellulose, the weight of water per weight of cellulose, the weight of the oil produced, and the percentage of oil found in various boiling ranges. The products from run W6-70-28 were very similar to those from the reaction with hydrogen without catalyst present, including the percentages of oil found in each boiling range.

The oils from the carbon monoxide (CO)-water reaction, the hydrogen only run, the water only run, and the HI run were all similar in qualitative composition. Although the quantitative analysis has not been completed, the preliminary work indicates similarities in several of these oils.

The amount of carbon monoxide and carbon dioxide found in the gas, when methyl iodide was used as a catalyst, was greatly reduced but the amount of oil was not appreciably increased.

The oil samples were run either on the Varian 1520 or on a Varian 1200 gas chromatograph which can be used in conjunction with the mass spectrometer. The mass spectrometer is a Varian M.A.T. CH7.

The columns used were each 20 feet long by 1/8 inch outside diameter aluminum tubing. One column was packed with 8% SE 30 silicone rubber on Chromasorb W 60/80 mesh. The other column was packed with 10% carbowax 20M on Chromasorb W 60/80 mesh.

The temperature was programmed according to the liquid phase and the boiling range of the oil. The crude oil was run on the SE-30 packed column, and the temperature was programmed from 50 to 200°C at 4° per minute.

Material Balance The material balance was examined for several of the runs, Table III. E. 4. If one looks at the oxygen balance, that is oxygen in versus oxygen out, one finds an oxygen loss for all hydrogenations except W6-70-23 and W6-70-27. Since the oxygen balance was primarily determined for the head gas and water, we must assume that the remainder (loss) is to be found in the oil. This is substantiated by the finding of aldehydes, ketones and phenols in the oils.

Run W6-70-23 is difficult to explain because of the large apparent gain in carbon. The carbon balance was determined by gas analysis and by calculating the oil to be totally composed of hydrocarbons. Any oxygen in the oil would therefore appear as an apparent gain in carbon in the oil. It becomes apparent that a full material balance is impossible unless the oil is quantitated for C, H, N, S, and O.

It does appear that the oil produced in run W6-70-27, hydrogenated in the presence of hydriodic acid, contains little oxygen. The 5.4% loss of carbon in the carbon balance may well fall within the limits of experim error for the handling techniques. The variations in carbon balance in runs W6-70-24, W6-70-26, W6-70-29, and W6-70-30 would indicate about 5% error was probable.

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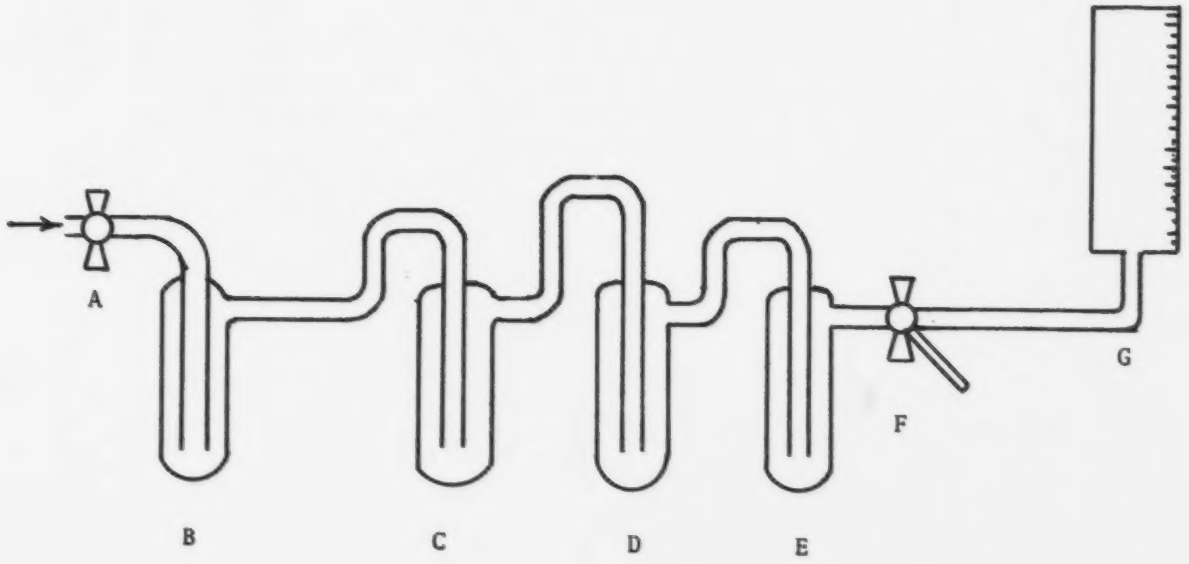

Figure III. E. 1. Gas Train for Analysis of the Head Gas from the High Pressure Reaction Apparatus.

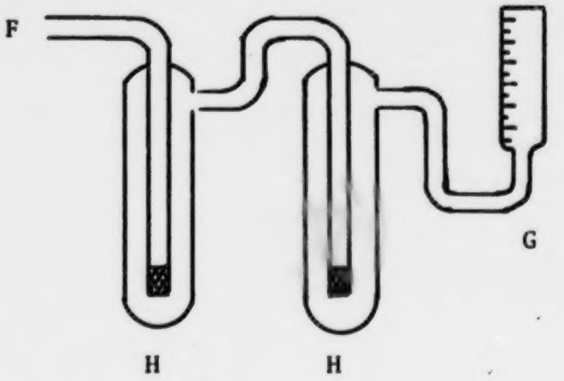

Figure III. E. 2. Carbon Monoxide Analysis System.

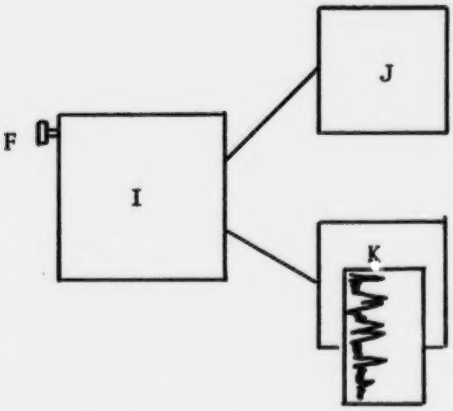

Figure III. E. 3. Gas Chromatographic - Mass Spectrometric Analysis System.

Table III. E. 1. Reaction Conditions and Products of Hydrogenations

	Hydrogenation Statstics				Gaseous Products (Moles/Mole of Cellulose)			
Run	Cellulose (g)	Gas (lbs)	Catalyst (ml)	Temperature (°C)	Hydrogen	Carbon Monoxide	Carbon Dioxide	Hydrocarbons
23	100	1000 H_2	None	370	1.32	2.42	0.398	0.208
24	107.7	950 H_2	25 CH_3I	355	0.085	0.663	0.405	0.995
25	92.7	None	None	395	0.001	0.001		1.46
26	93.7	950 H_2	None	375	2.98	0.332	0.955	0.526
27	94.9	850 H_2	25 HI	350	1.41	0.175	0.750	0.512
28	93.4	1000 CO	25 1% H_2CO_3	350	0.522	1.45	1.02	0.039
29	116.2	None	25 HI	370	0.158	0.219	0.560	0.329
30	93.1	None	50 H_2O	365	0.0	0.171	0.595	0.254
31	93.5	None	None	400				

Table III. E. 2. Showing the Amounts, in Grams, of Solid Residue, Oil and Water Produced per Gram of Cellulose Hydrogenated

Run	Residue	Water	Oil
23	0.347	0.157	-
24	0.341	0.236	0.013
26	0.316	0.175	0.066
27	0.179	0.374	0.135
28	0.318	-	0.079
29	0.585	0.069	0.008
30	0.392	0.107	0.016

Table III. E. 3. Information Received from Standard Oil Company Concerning A Sample of Oil From The Hydrogenation of Waste.

PROPERTIES	VOLUME PERCENT
Gravity, °API	31.3
Specific Gravity, 60°F	0.8692
Pounds per Gallon	7.24
Mixed Aniline Point, °F	90
Distillation, D-86, °F	
Initial Boiling Point	128 °F
5% Recovered	170
10% "	208
20% "	263
30% "	300
40% "	326
50% "	354
60% "	380
70% "	405
80% "	430
90% "	465
95% "	-
Dry Point	-

Table III. E. 4. Showing the Crudely Determined Material Balance of The Hydrogenation Reactions.

Material Balance

Run	Moles of Carbon in	Moles of Carbon out	Moles of Hydrogen in	Moles of Hydrogen out	Moles of Oxygen in	Moles of Oxygen out
23	3.70	4.81	5.91		3.08	3.00
25	.438	.441	3.92	4.19	3.32	2.021
26	3.46	3.201	4.66	3.07	2.88	2.201
27	3.51	3.32	6.66	6.55	4.17	4.20
28	6.29	4.45	4.26	1.71	7.11	2.853
29	4.30	4.47	5.36	1.94	4.83	2.26
30	3.44	3.67	5.65	3.84	5.65	4.01

Etherification

Methyl, ethyl, benzyl, and other ethers of cellulose are important in the production of textiles, cosmetics, medicines, films, and various plastic objects. For the product to be technically useful as a plastic item, it must regain a certain degree of hardness after being formed by fluid or plastic flow. Forming depends on applying the right conditions of temperature and pressure to the cellulose ether, which must have been formulated to give the desired properties to the product.

Some cellulose ethers may be considered to be, in a sense, internally plasticized by their constituents. The degree of internal plasticizing appears to be proportional to the size of the substituent group, and is quite pronounced in the case of the benzyl ether of cellulose. The higher alkyl ethers appear to have an increasing degree of softness and yet they exhibit an increasing tensile strength with the increased size of the substituent group.

The most common of the alkyl ethers of cellulose are ethyl and methyl cellulose. They are found in plastics, lacquers, sheeting, melts, varnishes, adhesives, therapeutic eye drops, and cosmetics. As plastics, they are useful as both soft and rigid plastics because they are tough. They find uses in both molded and cast objects. Some of the properties of methyl and ethyl cellulose are shown in Table III. F. 1. While varying degrees of substitution change the solubility pattern of these compounds, they can be made insoluble by crosslinking with bifunctional compounds such as: citric acid, glyoxal, and dimethyl urea.

Chemistry: According to Nikitin's interpretation (3:328-9) of the work of several authors. The mono-benzyl ether of cellulose is formed by treating cellulose with 15-25% sodium hydroxide solution and heating at 100°C with benzyl chloride. The use of 40-50% sodium hydroxide will form the disubstituted product if the reaction is started in a less concentrated base. This reaction is completed in less than eight hours at 100°C. At 130°C the reaction takes 2-3 hours.

The benzyl cellulose has a softening point between 145 and 170°C (293-338°F) depending on the properties of the product. Benzyl cellulose with a degree of substitution of 2.3 is used for the plastics industry (3:330).

The methyl ether can be made by treating soda cellulose with methyl chloride or dimethyl sulfate (4). The ethyl ether is made by essentially the same method (4). For both ethyl chloride, b.p. 12.2°C, and methyl chloride, b.p. -24°C, an autoclave is necessary to carry out the reaction without loss of the halide.

Mixed ethers have been prepared (1) by treating soda cellulose with mixtures of benzyl chloride and diethyl sulfate. The product is suitable for making filaments and films.

Cyanoalkyl cellulose is prepared by treating soda cellulose with acrylonitrile (2).

Carboxy ethers have been prepared (5) by treatment of soda cellulose with chloroacetic acid.

Hydroxy alkyl ethers have been prepared (6) from soda cellulose and ethylene oxide or chlorohydrin. These compounds are used in coatings, extrusions, and binders for pigments.

Experimental Results: Several samples of the benzyl ether of cellulose were prepared by treating soda cellulose with benzyl chloride under reflux ($T\sim 120$°C). The soda cellulose was prepared by soaking the cellulose in 30% sodium hydroxide aqueous solution for 1 hour. Soda cellulose made from Whatman #40 filter paper was treated with benzyl chloride for 2 hours to yield an orange product. This orange material was pressed at 300°F, 2000 lbs/in^2 for 4 minutes to form a hard disk without any indication of extrusion from the mold. A second experiment was conducted with the reaction time increased to 6 hours. Again the product was orange with an odor of aromatic compounds. On pressing, this material formed a yellow-brown translucent disk.

Straw was treated to form the benzyl ether by the same method. The reaction time was four hours. The product was pressed at 325°F for 4 minutes at 2000 lbs/in^2 to form a hard fibrous disk. From 10 grams of straw only 6 grams of product were recovered. The product from a second run using straw, when pressed at 325°F for 2 minutes at 1000 lbs/in^2, tended to extrude from the mold. Straw fibers were visible in this plastic.

A sample of sulfuric acid lignin was treated with sodium hydroxide followed by benzyl chloride in the same manner as noted earlier. When pressed, the product was bonded but did not flow. Fibrous particles were seen in this material also.

A sample of glucose was treated in the same manner. The product was a yellow liquid which would not crystallize.

Discussion: Several cellulose ethers are used commercially at present. If these are used for plastic molding or casting purposes there is reason to believe that the purity of the cellulose source does not have to be exceedingly high for many of these products.

Pure cellulose, in the form of filter paper, appears to give a product in which the plastic properties can be controlled more easily than with the impure straw. The benzyl ethers of sugars in the straw are thought to be the cause of the increased plasticity and flow properties of the second run.

When glucose was treated, the benzyl ether was recovered as a yellow oily substance which would not readily crystallize. Such a material could easily act as a plasticizer.

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Table III. F. 1. Some Properties of the Methyl and Ethyl Ethers of Cellulose.

Degree of substitution	Property
Ethyl	
2.60-2.8	Soluble in hydrocarbons
2.20-2.58	Thermoplastic; soluble in common organic solvents
.8-1.7	H_2O soluble; difficult to control
Methyl	
2.4-2.8	soluble in polar organic solvents
1.6-2.0	soluble in cold H_2O
.1- .9	soluble in 4-10% of NaOH

Made insoluble with crosslink by bifunctional compounds.

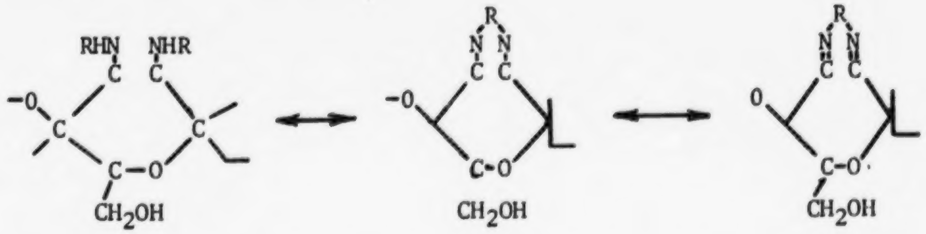
Oxidation of Cellulose

Because of the similarity, in respect to chemistry, between dialdehyde cellulose (DAC) and dialdehyde starch (DAS), derivatives of dialdehyde starch have been included in this report. One finds upon examination of the literature that most of the derivitive preparation has been done with DAS, but structural examinations through infrared spectroscopy have been carried out on DAC. DAC and DAS seem to undergo all of the reactions typical of aldehydes. DAS is commercially prepared by The Miles Chemical Works using an electrolytic production of periodate.

Several reactions of dialdehyde polysaccharides (DAP) with nitrogen compounds have been studied. Kuznetsova et al. (23) reacted DAC in aqueous solutions at room temperature during 24 hours, or at the boiling point of the mixture in 4 minutes, to give a series of amino compounds. Thermal stability varied, but generally decreased in the following order:

$$m - p - (H_2N)_2C_6H_4 > N_2H_4 > o - (NH_2)_2 C_6H_4$$

The structure of the products was determined to be



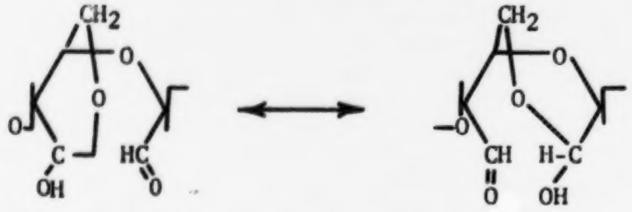
Ia Ib Ic

Roqovin et al. (35) reacted DAC with aromatic amines to synthesize Schiff-Type bases (Ic above) which were useful in preparation of chemically colored cellulose fibers from various diazo compounds. A patent (39) exists for the condensation of o-aminophenol with a dialdehyde. This type of compound is useful as tuberculostats and intermediates for the preparation of medicines and dyes.

Patents exist on the reactions of DAP with melamine and other triazines. The uses so far have been in papermaking. These reactions impart wet strength and dimensional stability to paper.

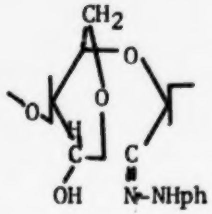
Honeyman and Holker (18) reacted DAC with several amines and hydrazine derivatives, but reported the reaction to be incomplete in all cases. The products remained alkali sensitive making them of no value to the textile industry. Material treated with urea was wrinkle and flame resistant, while the thiosemicarbazide is resistant to attack by most fungi.

DAC undergoes reaction with the hydrazides. With phenylhydrazine a phenylformazan, IIc, is formed showing that the DAC reacted to give one of the two possible hemi acetals, IIa and IIb, (28).



IIa IIb

Hemi-acetal forms



IIc

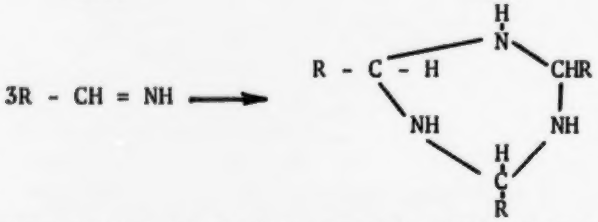
formazan

DAS has been left standing in liquid ammonia to produce a compound containing two nitrogen atoms per dialdehyde unit (40). The product decomposed on standing, because of the unstable nature of the α-amino alcohol, IIIa, formed. It is possible for the reaction

$$\underset{\text{IIIa}}{RCH(OH)NH_2} \xrightarrow{-H_2O} \underset{\text{IIIb}}{R - CH = NH}$$

to occur. From IIIb one can obtain IIIc.

IIIb IIIc



The dioxime of DAC is readily formed. Reduction of the dioxime gives the amine, while dehydration gives the nitrile. A literature search has not revealed the formation of the nitrile from DAC using the cyanide ion.

Rogovin (36) states that the diamino derivatives, from the reduction of the oxime, can be used to initiate grafting of monomers, particularly of the cyclic type.

DAP acetals have been produced and are used in coating and laminating applications. DAP-phenol derivatives (29) are used in resins and adhesives. Several patents (2, 3, 5, 22) cover the production of dialdehyde polysaccharide-urea resin. These products have applications as adhesives, wet strength agents for paper, and textile finishing agents. The resin formed is a thermo-setting resin. A casein-DAS resin has been prepared and tested for use as a plywood bonding agent (42).

A general reaction of aldehydes with epoxides (40) might be found to be useful, since a patent covering aldehyde-epoxide copolymers formation using poly(hydrocarbyl aluminum) catalyst does exist. A flexible thermoplastic resin has been prepared by the reaction of 1,2:5,6-diepoxycyclooctane with adipic acid (12). Other resins can be prepared by using difunctional compounds such as diamines and dialdehydes.

Difluoramine dialdehyde cellulose is used as an energetic constituent of rocket propellants with the reduced form being more stable (21). The difluoaminated cellulose compounds are prepared by reacting DAC with liquid difluoramine in an inert atmosphere using an acid catalyst such as sulfuric acid (45). The Russians hold a patent for the preparation of fluorine containing cellulose derivatives. The cellulose is reacted with sulfur tetrafluoride in the presence of sodium chloride.

Livshits and Rogovin (24) have developed a system of graft copolymerization without the simultaneous formation of homopolymers. The system consists of a polymer containing reducing groups, a suitable monomer, and a pentavalent vanadium compound as the oxidizing agent. Successful graft copolymers were: DAC/polyacrylonitrile (PAN); a cellulose derivative containing aromatic amine/PAN; and the same cellulose derivative/poly (2-methyl-5-vinyl pyrimidine). Methylmethacrylate and methyl acrylate grafting to DAS was studied by Ide and Nakatsukak (19). Bochert patented (4) a grafting method for DAS and acrylamide.

Cellulose peroxide (6) has been prepared by oxidizing DAC with hydrogen peroxide. The peroxide decomposes to free radicals which can be used to initiate graft copolymerization.

Other reactions of DAC include the introduction of disulfide crosslinks by reaction with acethydrazide disulfide (17), the preparation of nitrate and acetate esters (44), the reaction of DAC with trialkyl phosphates (30), the polyazine formation from the reaction of N_2H_4 (25), and bis (amidinohydrazone) from aminoguanidine (20).

Possible uses of DAC mentioned in the literature are as a fuel filter (33), and the thiosemicarbizide has the ability to fix metal ions such as copper, cobalt, silver, mercury, nickel, lead, and iron to yield colored compounds (34) for dying or as an indicator for these metals.

Chemistry: Oxycelluloses differ from cellulose by their higher content of oxygen due to increased carboxyl and carbonyl content. The oxycellulose obtained by the oxidation of cellulose in acidic or neutral media are, usually, of the so called reducing type and contain large numbers of carbonyl groups. When cellulose is oxidized under alkaline conditions the oxidation generally proceeds to the carboxyl stage.

Periodic Acid and Metaperiodate These oxidants lead chiefly to dialdehyde-cellulose (DAC), but studies show a partial oxidation of the C-6 hydroxyl to the aldehyde and carboxyl groups (about 10% of the total oxidized hydroxyl units) (31).

The CO_2 yield and increased weight loss noted with increasing degree of oxidation are considerably greater for periodic acid than for metaperiodate oxidations (7). Periods of a week or more are necessary for production of a high degree of oxidation in cellulose. Acid hydrolysis does not play an important part in the oxidation of cellulose by periodic acid. The possibility of acid attack during the metaperiodate oxidation is ruled out by the low hydrogen ion concentration in the metaperiodate solutions.

The properties of dialdehyde cellulose are markedly different from those of cellulose, for instance the strength of the dialdehyde cellulose is slightly lower than that of cellulose. Periodic acid oxidized cellulose shows an increased hygroscopicity over that found in cellulose. Treatment of cellulose sheets with periodic acid results in pronounced shrinkage in area, but increased thickness. The introduction of two aldehyde groups into the anhydroglucose unit of cellulose produces considerable decrease in stability of the glucosidic bond to the action of alkali. All of these differences are brought about because the periodate ion can penetrate the ordered as well as the disordered areas of cellulose to produce the dialdehyde cellulose. The production of periodate oxidized cellulose can be found in references 14, 15 and 43.

Preparation of metaperiodate solution is accomplished by adding sodium hydroxide to periodic acid in the proportion of one mole of base to one mole of acid, or by dissolving recrystallized salt in distilled water. The final solution used in the oxidation of cellulose to dialdehyde cellulose is usually 0.1 Molar in metaperiodate.

Lead Tetraacetate Lead tetraacetate in glacial acetic acid oxidized glycols to pairs of carbonyl groups at rates which were greater for cis than trans configurations and were dependant upon the particular glycol.

Detrick (9) made a thorough study of the oxidation of wood pulps by $Pb(OAc)_4$ and found that there was a selective oxidation of mannose units. In addition, a smaller but significant removal of xylose units occurs. In his oxidation of pulp, Detrick treated dry pulp with acetic acid at 50°C to activate the pulp. Preheated lead tetraacetate in glacial acetic acid was then added and the reaction allowed to proceed. Ten hours was found to be about the minimum reaction time. The reaction was quenched using a solution of potassium iodide, and sodium acetate in distilled water. Quenching can also be accomplished using oxalic acid.

The type of pulp used, affects the length of time needed to reach a certain level of oxidation. A minimum of about seven hours is required to reach 0.2 atoms of oxygen consumed per anhydroglucose unit.

Abdel-Akher (1) oxidized various polysaccharides using a lead tetraacetate and sodium acetate solution. The reaction mixture was kept in the dark at 25°C for 15 - 45 days with an occasional shaking and addition of lead acetate. The insoluble residue was removed by centrifugation, washed with acetic acid, water, ethanol, acetone, and ethyl ether, then dried in vacu to give 88 - 95% partially oxidized polysaccharide. With cellulose he achieved 17.21% dialdehyde units.

Vargha (41) states that red lead, Pb_3O_4, can be used in many cases to replace lead tetraacetate.

Peroxydisulfate Heidt (16), in a review article of the oxidation of cellulose to dialdehyde cellulose, indicates four possible oxidants: periodate, lead tetraacetate, peroxydisulfate, and perbismuthate. At the time of the article (1945) no work had been reported using peroxydisulfate. A review of the literature by Menghani (27) in 1969 indicated that the oxidation of diols by persulfate had not been reported. A literature search has not turned up any reported work since that time.

Rusznak, Kantouch, and Khalil (38) studied the oxidation of cellulose with sodium persulfate at 50-70°C, pH 4 - 10, and with solutions of persulfate ranging in strength from 0.05 - 0.3 N. The oxygen consumed (determined by titration with acidic ferrous sulfate) in the oxidation increased with increasing time, pH, temperature, and persulfate concentration. At pH 8 and 70°C, oxygen was released faster than the rate of oxidation of cellulose with a subsequent evolution of oxygen.

Work done by Menghani (27) indicates that in the oxidation of ethanediol using persulfate with silver ions as catalyst, the rate of persulfate disappearance depends on both the persulfate and silver ion concentrations.

Oxygen causes an inhibition period with peroxydisulfate which is dependant on the amount of dissolved oxygen present.

Perbismuthate Perbismuthate is a rapid acting oxidizing agent, but there is a drawback to its use with cellulose: Perbismuthate is a relatively insoluble brown powder, whose reduced form $Bi(OH)_3$ is also poorly soluble. These properties render perbismuthate of little value for use in oxidizing cellulose or other insoluble substances (16).

Chromic Acid and Chromic Anhydride The early stages of the oxidation of cellulose by chromic acid produces dialdehyde cellulose.

Cotton oxidized by chromic acid falls into a powder when the oxygen consumption reaches about 0.4 atoms per anhydroglucose unit (8). Chromic acid oxidation does not lead to marked swelling as does the periodate oxidation. Chromic acid confines its attack to the disordered regions of the cellulose fiber. It also leads to an increase in hygroscopicity which is not as high as in the periodic acid oxidations. Both chromic acid oxidized and periodate oxidized cellulose show a decrease in tensile strength, but in the latter stages of oxidation the chromic oxidized cellulose has a much lower tensile strength (32).

Feher (10) proposed an industrial application of electrolytic oxidation with chromic acid of starch using the method of Mehltratter and Wise (26), but found the method inconvenient. He then proposed the use of potassium dichromate in strongly acid medium. The product contained 60% dialdehyde and only 4 - 5% -COOH groups.

Gladding and Purves (13) did an extensive study on the use of chromic anhydride dissolved in acetic acid-acetic anhydride, and in sulfuric acid, on cellulose. The acetic acid solvent was found to be more efficient in producing carbonyls and about 10 times faster than sulfuric acid solution.

t-Butyl Chromate Oxycelluloses containing aldehyde groups in the C-6 position are prepared from cellulose or partially substituted cellulose, at 20 - 70°C, in an acetic anhydride solution of of t-butyl chromate (37). The fibrous products are white and stable when stored in the absence of light and oxygen. They are useful for surface coatings and finishes on textiles through cross-linking reactions.

Hypobromite Oxidation of cotton by hypobromite in concentrated alkaline hypobromite solutions is non-selective and approaches wet conbustion (11).

Hypochlorite In alkaline solutions, where the effective oxidant is the hypochlorite ion, the reaction is very slow and gives rise to an acidic oxycellulose with little reducing power (43). In mildly acidic solution, pH 3 - 5, in which the effective oxidant is undissociated hypochlorous acid, the reaction is again slow but gives rise to a highly reducing oxycellulose containing few acidic groups. In neutral solutions the rate of reaction is at its maximum, and oxycelluloses with both acidic and reducing properties are produced.

Hydrogen Peroxide Oxidation by hydrogen peroxide is essentially the same as hypochlorite, but during the oxidation of cellulose the glycol grouping at C-2 and C-3 are attacked simultaneously, resulting in the formation of two aldehyde groups (43).

Nitrogen Dioxide Nitrogen dioxide is a more or less specific reagent which oxidizes primary hydroxyl groups in cellulose to carboxyl groups (31). Cellulose may be oxidized by gaseous nitrogen dioxide, by the liquid tetroxide, or by solutions of nitrogen tetroxide in inert solvents.

Chlorine Dioxide Chlorine dioxide, in acid medium, does not react with cellulose (31), however in any other media it leads to oxidation of aldehyde groups to carboxyl groups. This oxidation involves both the terminal hemiacetal groups and aldehyde groups formed by the oxidation of cellulose by other oxidizing agents.

Experimental Results: There are several oxidative materials that may be used to produce dialdehyde cellulose. For several reasons, we elected to work with periodate, chromic acid, and persulfate oxidations first. Periodate oxidations are well documented and there is little doubt that it is fairly specific for vicinal hydroxyl cleavages. Nikitin

(31) does note however, that about 10% of the primary (C-6) hydroxyls are oxidized during the reaction.

Basically, there are two ways of determining the degree of oxidation of the sample: by measuring the fall in the concentration of the oxidative material, or by reacting the carbonyl units in the product with a reagent that is specific for such groups. Neither method appears to be exceedingly accurate. The decrease in oxidative agent does not mean that only the aldehyde is formed nor are many aldehyde specific reagents completely reacted because of the stereochemistry of the cellulose. Hydrolysis of the cellulose to glucose units would obviously lead to higher yields of oxime because of additional aldehyde units available.

Chromic acid oxidation is not as selective as the periodate method, but a comparison was run using the method of Whistler (43).

A comparison of our kinetics and those of Whistler was made. Whistlers method was modified by buffering to pH = 5 by the addition of acetic acid and sodium acetate for use with samples 1 and 2. A large discrepancy was found between the oxygen comsumption and the amount of carbonyl present by oxime formation for samples 1 and 2, Table III. G. 1. An interesting phenomenon is the apparent increase in periodate concentration in the first two days. This work was not repeated to confirm this observation.

The large amount of hydroxylamine consumed in oxime formation for samples 1 and 2 indicates oxidation of the C-6 carbon probably took place.

Table III. G. 2. contains the results of the persulfate oxidation experiments. Ammonium persulfate was used as the oxidizing agent, and the reaction times ranged from 15 minutes to two days using various catalysts. The most noticable change was the loss of weight of the cellulose. Oxime analysis indicates few carbonyl groups were formed. The pH was maintained at 2 except when a buffer was added. At a pH of 2 one would expect hydrolysis of the cellulose to glucose which probably accounts for some of the weight loss.

The chromic acid hydrolysis was carried out using the method of Whistler (43). Figure III. G. 1. shows the oxygen consumption versus the reaction time. Table III. G. 3. gives the data from this work, comparing the titrametric (oxygen consumption) analysis with the analysis by oxime formation. One can readily see that the data indicates carboxy unit formation rather than carbonyl formation.

Alkaline degradation of the oxidized cellulose was observed when the pH was allowed to become too high during oxime formation.

Discussion: There are a number of oxidizing agents capable of converting cellulose to dialdehyde cellulose (DAC) or carboxyl cellulose. At present there are not enough uses known for this substance to justify spending much time examining this process.

The conversion of cellulose to DAC has many interesting possibilities if the reaction rate could be increased to make the process economically feasible. DAC, made from waste paper, could possibly be used as the basis for resins for water purification, for resins to be used by the plastics industry, paint industry, and many other applications.

Because of the long periods of time needed for the formation of DAC, this material was only briefly examined in this laboratory.

Cellulose peroxides were not examined, but hold a special interest because of their potential use as initiators for graft polymerization.

In general the formation of DAC was found to be better with the periodates, as the literature suggested, than with other oxidizing agents. However at present this does not look like an economically feasible method for handling the large quantities of wastes necessary for the solution of the problems of pollution in this country.

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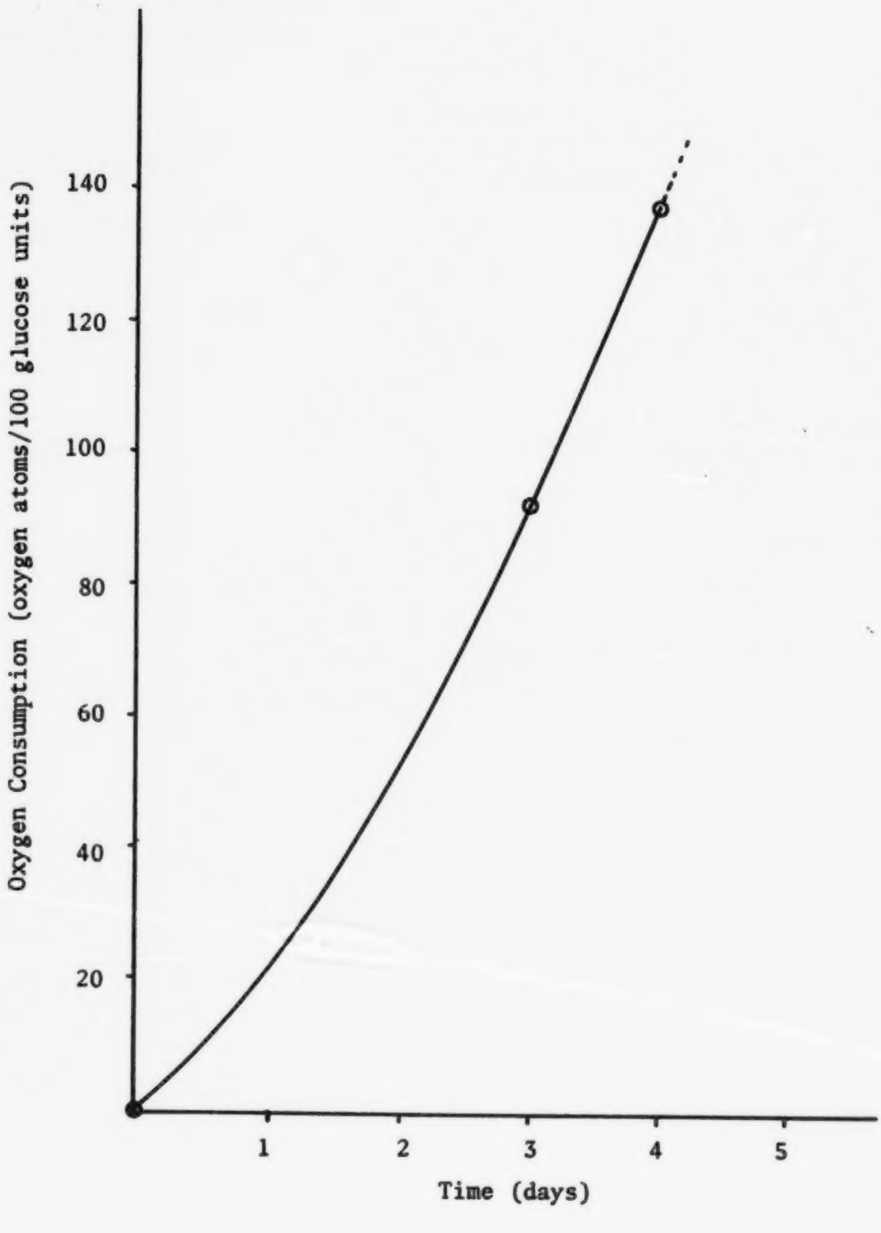

Figure III. G. 1. Showing The Oxygen Consumption With Time in The Chromic Acid Oxidation of Filter Paper.

Table III. G. 1. Periodate Oxidation

Sample I 10g filter paper; 1 N $NaIO_4$; 1 liter of soln; 2/7/72-2/17/72

20 mls of HOAc-NaOAc buffer pH 4.

Days	1	2	3	4	5	6	7	8	9	10
Oxygen Consumption		1.8	6.9	11.1	-	-	21.4	-	24.7	25.7
% Conversion (Oxime)										>100%

Sample II 20g paper; 5 N $NaIO_4$; 1 liter of soln; 2/7/72-2/17/72

20 mls of HOAc-NaOAc buffer pH 4.

Days	1	2	3	4	5	6	7	8	9	10
Oxygen Consumption			.9	2.6		-	7.8	-	9.9	10.8
% Conversion (Oxime)										>100%

Sample III 20g paper; 5 N $NaIO_4$; 1 liter of soln; 2/8/72-2/21/72

no buffer

Days	1	2	3	4	5	6	7	8	9	10	11	12	13
Oxygen Consumption	2.9	5.0	6.4	-	-	9.2	-	10.6	11.2	--	--	--	13.2
% Conversion (Oxime)													77%

Table III. G. 2. Persulfate Oxidation

Time (min)	pH	Catalyst	% Conversion	Weight Loss (gm)
20	2	Ag^+	0	0
30	2	Ag^+	0	0
60	2	Ag^+	0	0
120	2	Ag^+	6.2	.3
2 days	2	Ag^+	-	.1
120 min	2	Fe^{+3}	0	.33
120 min	2	-	0	0
15	4	Ag^+	0	0
30	4	Ag^+	0	0

Table III. G. 3. Chromic Acid Oxidation

10g paper; 30gm $Na_2Cr_2O_7$ & 11 mls conc. H_2SO_4 per liter; 2/4/72-2/9/72

Days	1	2	3	4
Oxygen Consumption	-	-	92.6	136.8
% Conversion (Oxime)				15

Pulping of Straw

For many years straw was pulped in this country, and in other countries it is still pulped. Why is straw no longer used for pulp in this country? Some sources say that the straw pulp mills would not modernize, while this did not impair the quality of the product, the cost per unit of product was forced upward until these mills priced themselves out of existence. Others say that straw storage is too much of a problem.

With our forests being depleted the time has come to re-evaluate straw and waste paper as a source of pulp. If this pulp is unsatisfactory for paper it may still be satisfactory for cardboard cartons, chemical intermediates, or wrapping paper.

The Institute of Paper Chemistry (9) has compiled a bibliography listing articles and books covering cereal straws as a source of cellulose for papermaking. The original publication has been supplemented twice (7) (8). These articles are primarily concerned with papermaking and not with growing, harvesting, economics, or extraction of the straw.

Straw can be pulped by nearly any pulping process, however, these are not necessarily economical. The high silica content of straw can cause problems in boilers, while the low bulk density can reduce equipment capacity.

Straw lignins can be removed from the cellulose by nitric acid pulping or by the soda process. Laboratory evaluation has shown that both of these methods are effective in producing pulp from grass seed straws. A third method, holopulping (5), which is supposed to have less pollution than the Kraft process has not been investigated yet.

Chemistry: There are several methods available for pulping cellulosic materials, among these are the sulfite process, the sulfate (Kraft) process, soda process, nitric acid process and the holocellulose process.

Nitric Acid Pulping — The nitric acid pulping process (1), (2), (3), (4) consists of treating straw with hot nitric acid to oxidize and nitrate the lignin. The lignin is then dissolved by a dilute sodium hydroxide solution.

In the laboratory bentgrass and fescue straw treated with 10% nitric acid at 70°C for 1 hour followed by a 2% sodium hydroxide treatment for 1 hour at 90°C resulted in 29% and 30% pulp respectively. Three similar runs with annual ryegrass resulted in an average yield of 26%. Because less concentrated acid should result in less degradation, a series of runs were made to determine the effect of nitric acid on the pulp yield. The alpha cellulose content of the pulp from each run was measured. These results are shown in Table III. H. 1., and Figure III. H. 1. As expected, the pulp yield increased with decreased acid concentration.

Linear extrapolation to zero nitric acid concentration indicates that sodium hydroxide alone should result in a 41.5% yield of pulp with 83.5% alpha cellulose.

Sodium Hydroxide Pulping In a series of runs straw was pulped in 1N, 3N, and 6N sodium hydroxide at 70°C for 1 hour. The resulting pulp yields were 38.5, 38.2 and 35.7% respectively. Another sample was treated with 1N sodium hydroxide for 2.5 hours at 70°C. The pulp yields for all runs are shown in Table III. H. 2. The 6N sodium hydroxide treated straw became gummy and hard to handle.

The Forest Research Laboratory of The School of Forestry at Oregon State University then did some additional work with straw using the "Soda Process" (4). They reported yields between 50% and 60% using 16% (4N) chemical. The tensile, burst, and fold strengths compared favorably with the commercial soft wood Kraft papers.

Discussion: As stated earlier, pulping can be accomplished by the use of one of several methods. The "soda process" has been shown to be satisfactory for making pulp from straw. Because the use of sulfur compounds has been eliminated there is practically no smell to mills using the soda process. The holopulping process which was not examined in this laboratory reportedly (5) is more economical than the Kraft process.

The main drawbacks to using straw are all expressed in economic terms. The information from pulping of grass seed straws is minimal. More work in this area, improved techniques for handling and storing straw, and the dwindling forests may soon bring straw back into the field of pulp production.

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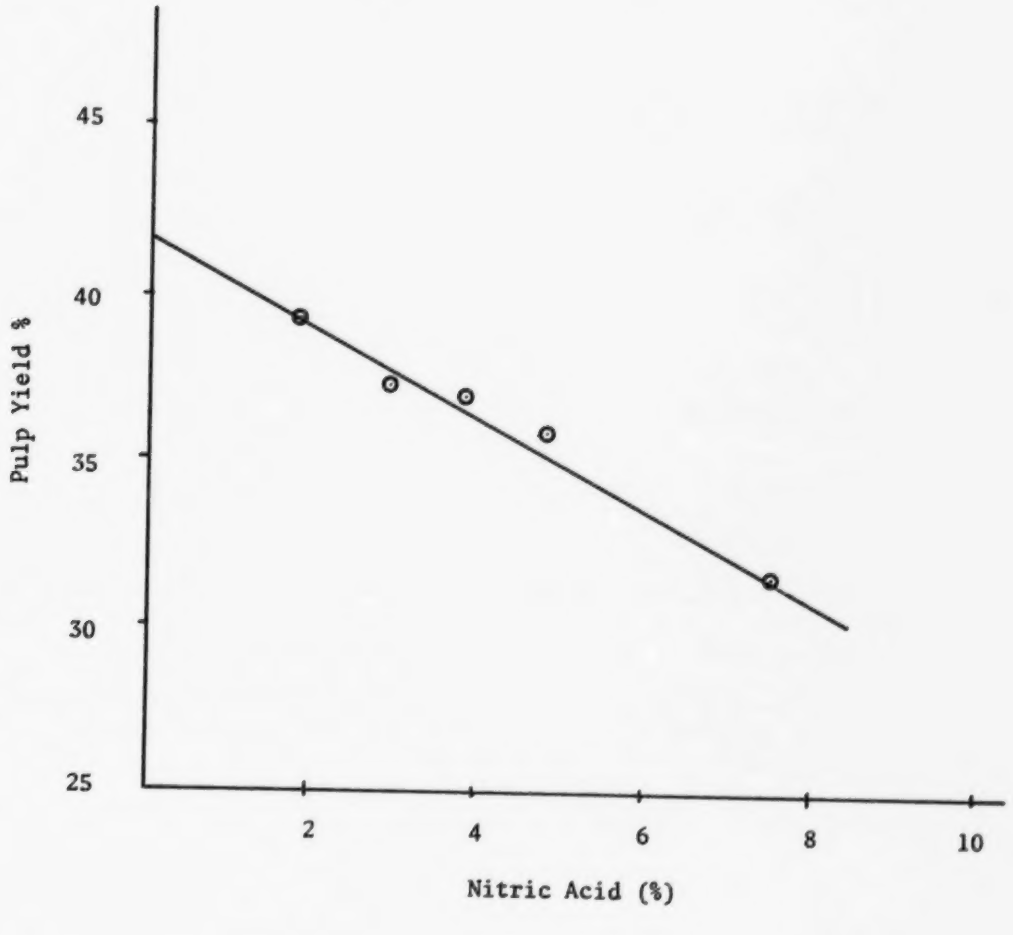

Figure III. H. 1. Showing The Reduced Yield with Increased Acid Concentration During Nitric Acid Pulping.

Table III. H. 1. NITRIC ACID PULPING OF ANNUAL RYEGRASS STRAW

Run	A	B	C	D	E
Wt. Dry straw, gms.	100.0	100.0	100.0	100.0	100.0
Concentration HNO_3, wt. %	7.5	4.8	3.8	2.9	1.9
Reaction time at 80°C, hrs.	1	1	1	1	1
Concentration NaOH, wt. %	2.0	2.0	2.0	2.0	2.0
Dissolving time at 90°C, hrs.	1	1	1	1	1
Wt. Pulp, gms.	31.5	35.9	36.8	37.3	39.2
Pulp yield, dry basis, %	31.5	35.9	36.8	37.3	39.2
Alpha cellulose, %	85.5	84.5	84.7	84.5	84.0
Beta cellulose, %	10.4	9.4	7.6	8.1	8.0
Alpha cellulose yield, %	26.9	30.3	31.2	31.5	32.9

Table III. H. 2 Sodium Hydroxide Pulping of Straw

Run	NaOH Conc. (N)	Cooking Time (hr.)	Cellulose yield (wt. %)
1	1	1	38.5
2	3	1	38.2
3	6	1	35.7
4	3	2.5	42.5

PILOT PLANT STUDIES

Economic and Engineering Analysis

Each year industry produces thousands of products which are useful in society, but when they lose their usefulness they become solid waste, which must be transported to a disposal site. In the the early years of our country, when the population was sparce, it was easy to find disposal sites. Today serious waste disposal problems exist because disposal sites are no longer readily available and the amount of waste is increasing because of our increased population and our convenience packaging of consumer goods. Improper disposal methods have contributed to environmental pollution. It is essential that we develop and utilize acceptable waste management systems.

One alternative to the present method of burial and burning is reutilization of our wastes. A large portion of our wastes should be treated as raw materials for the production of new, usable products. Using solid wastes as raw materials would conserve our natural resources, and at the same time reduce the amount of waste that needs disposal.

Although the main economic factors of the reutilization processes are the Capital Investment and The Total Product Cost, other economic factors to be considered when waste is involved include: resource conservation, social resistance to change, industry survival, and environmental pollution. These factors will be discussed in relation to a process designed to use waste straw to make a solid particleboard through isocyanate crosslinking.

Crosslinking: Straw, the hollow stalks or stems of some agricultural crops, is a solid waste of agriculture; more specifically, in Oregon, straw is a solid waste of the grass seed and cereal industries. When the grass seed or cereal grains are harvested, the straw is normally left in the field. When the straw is not subsequently removed. a reduction in crop yields usually occurs the subsequent year. Straw can be removed by bailing or by tilling (plowing under) with two exceptions; perennial crops are not tilled for the life of the stand, and some heavy clay soils inhibit the normal degradation processes, (undecomposed straw has been unearthed after 2 years of burial).

In the mid 1940's when blind seed fungus (Glocotima temulenta) was infecting 90% of the perennial ryegrass crop of Western Oregon, open field burning was recommended as a field sanitation measure (1). Burning proved to be effective in controlling disease and served as an inexpensive means of residue disposal. In addition, burning served to kill weed seeds on the soil surface, reduce fertilization requirements, increase seed yields, reduce fire danger, partially control insects and rodents, and release minerals back to the soil. This practice was later adopted for other crops as well, until in 1970, approximately 300,000 acres were burned.

The major disadvantage of open field burning is that it contributes to air pollution. According to a study by Boubel (1), particulate emissions average 15.6 lb/ton of fuel burned. Carbon monoxide, hydrocarbons, and nitrogen oxides are also produced. Normally, these products would be dispersed in the upper atmosphere, but meterological studies have revealed that the climatic conditions in the Willamette Valley are not always conducive to smoke dispersion (3:23). During these times, particulate and gaseous emissions are held near the ground, resulting in decreased visibility and increased human annoyance.

The increasing acreage and tonnage of crop residue being burned, coupled with the increase in population and the limitations of natural atmospheric ventilation in the Willamette Valley, have led to a legislative decision to ban field burning after January 1, 1975. This decision will necessitate the development of alternative cultural practices for field sanitation if Oregon is to retain its position as a major world supplier of grass seeds. In 1968, Oregon produced 41% of all U.S. grass and legume seeds on 308,000 acres at a sales value of $31 million. Eighty one percent of this was produced in the Willamette Valley. Virtually all of the U.S. ryegrass production is from 134,000 acres in the Willamette Valley. This yield has a value of nearly $13 million (2).

A state supported research program is being conducted at Oregon State University to develop alternative cultural practices to replace open field burning. One alternative is the use of a mobile field sanitizer, a machine capable of burning crop residues with less resultant air pollution, but the physical removal of some of the straw will probably be required. The industrial utilization of this straw for the production of useful products will conserve a natural resource, provide an acceptable disposal method, and could provide the farmer with an economic return to help defray the added costs of straw removal. Denmark (4) has studied the production of a straw particleboard, and since straw particleboard is one product with potential for industrial utilization in home construction and finishing, furniture, and decorative articles, this process is being studied at Oregon State University as part of a research program supported by the Environmental Protection Agency, State of Oregon, and Oregon Seed Council.

Engineering Factors This analysis is designed to identify the major factors that contribute to the total product cost. A capacity of 100 tons/year of product has been selected to provide information for a small pilot plant. This size of plant could be operated by two employees using readily available equipment and the product could be used to evaluate physical properties and to determine market potential. Operative information could be used for scale-up analyses. Since it is anticipated that modifications will be proposed to reduce both capital investment and total product cost, this analysis is presented as a starting point for the development of a process to utilize waste straw.

A schematic design of the process is shown in Figures IV. B. 1. and IV. B. 2. The plant would be constructed in a 40' x 40' steel building on a concrete pad. Adequate storage area is available for the year's supply of straw.

The straw will be removed from the field and stored in 50-pound bales, held with 2 strands of wire or string. The straw will be fed into a mill. The milled straw will be carried by air to a cyclone separator where the straw will be collected and the air will pass out of the top carrying the fines. The fines will be collected in a bag.

If drying is required prior to the resin application, the straw will be fed through a dryer and into a rotary mixer for the resin application. Scales will be used to determine the resin concentration. Liquid resins such as polyisocyanates, U. F., and P. F. will be applied by spraying with compressed air. Solid resins such as acrylics or bakelite will be physically mixed prior to pressing. The straw/resin mixture will be pressed into a solid particleboard with a heated platen press. The density and size of the board will be determined by the quantity of straw used and the pressure. The board will be cut to finished size with a saw and a finish coat will be applied if desired. The waste material will be returned to the mill for recycling. The finished product will be stored for later utilization.

The following equipment is readily available for utilization in the plant with a capacity of approximately 100 tons of product/year.

A hammermill of the type similar to a Ward's Model 6A hammermill with a changeable screen is adequate for reducing the straw particle size. It has an approximate capactiy of 150 pounds/hour. The straw is carried by air to a cyclone separator where the chopped straw is collected. A cloth bag can be utilized to filter the dust from the air. Approximate cost, $260.00.

The dryer may be a rotary drum, fluid bed, or tray dryer, a more economical way of drying might involve circulating hot air through the cyclone separator. The heater, fan, and ducts could be fabricated for less than $50.00. The dryer is left out of this schematic because laboratory experimentation indicates that for some resins, the presence of water vapor is not detrimental.

The mixer can be any one of several types of commercially available ribbon blenders or rota-cone blenders with sprayers which can be used to achieve a good spray coating of resin on the straw particles. This equipment is available in both small and large sizes but a suitable size for this plant would cost approximately $5,000.00. Continuous resin application would be possible using a Day Centri-Flo mixer® which can process over 600 pounds/hour.

A direct reading scale would be utilized to determine the resin concentration. Since batch sizes would be approximately 5 pounds or multiples thereof and resin concentrations could vary from 5 - 10%, a 10-25 lb. scale with 2 ounce markings or 0.1 pound markings would be needed. Only one scale would be needed with a container for transferring the straw from the cyclone to the mixer and from the mixer to the press. Approximate cost, $50.00.

An automatic hydraulic press with heated platens 24.5 inches square would be ideal for producing a 24 inch square board, however, the cost would be over $8,000.00. Manual presses are not available as a stock item at this size. Although normally a one-opening press, alterations could be made to convert it to a multiple opening press in order to increase its capacity.

A small table saw could be used to cut the boards to finished dimension; approximate cost, $50.00. The waste scraps would be fed back into the process at the mill. The finished product would be stored for transportation to a sales center or for utilization in making straw particleboard products.

The equipment mentioned here would be useful for a manually operated batch pilot plant. A study of the results of variations in process variables on the properties of the product could be conducted, and the design for a larger automated plant could be established. In addition, a market study could be conducted to determine the market value of the product.

Economic Considerations The industrial utilization of straw would be greatly enhanced if a profitable process could be developed. Profitability depends primarily on the cost of processing and the value of the product. It is important to identify the contribution that the various aspects of processing make to the total cost so that efforts can be made to reduce the total cost of processing. It is also important to identify the value of the product in its most likely applications. This may necessitate the production of finished products for retail sales evaluation.

A sample estimation of fixed capital investment and total product cost for a 100 ton/year pilot plant using polyisocyanate resin is given in Table IV. B. 2. and Table IV. B. 3. No additional equipment would be needed to produce boards with other resins. This plant would be manually operated by two men.

Indirect costs and general expenses are estimated based on the assumption that this plant would be a part of a larger business enterprise requiring some supervision and overhead expenses. If, for example, ten such plants were located near grass seed farms to reduce transportation costs, supervision, clerical, sales, and maintenance support could be shared. These costs, then are listed at 1/10 of the total estimated cost for the larger business enterprise.

The plant would be operated for 8 hours/day and 250 days/year. Since capacity is rated at 200,000 pounds of product/year, the average daily production rate would be 800 pounds or 100 pounds/hour.

The unit production cost is estimated at $0.15/lb product or $4.80 for a 4' x 8' x 1/4" sheet with a density of 48 lb/ft^{-3}. If the press could be modified into a multiple opening press with no change in capacity or operating cost, the cost for a sheet 4' x 8' x 1/8" could be reduced to $2.40.

The value of a straw particleboard made with polyisocyanate resin has not been determined as yet, however, it has general appeal for use as decorative interior home paneling. The cost of wood paneling ranges from \$2-8 for a 4' x 8' x 1/8" panel depending on quality and finish.

The value of straw particleboard for utilization in lamination or furniture construction is difficult to estimate without a market survey using actual samples, however, it is presumed that consumer acceptance will be sufficient to establish a value higher than the estimated production cost, even though the margin of profit will be low at this production rate. The unit production cost could be lowered by automation and by increasing plant capacity through the use of larger machines since operating labor accounts for 47% of the total product cost. The use of lower resin concentration or a different, less expensive resin, assuming no change in physical properties, would make a slight reduction in the production cost since resin costs account for 15% of the production cost. The cost of the straw accounts for only 6% of the cost of the product.

Resins Examined In the laboratory, six different resins have been received in order to evaluate the preparation of a solid board from straw; bakelite, acrylic, transoptic powder, phenol-formaldehyde, urea-formaldehyde, and isocyanate. The resin cost and the physical properties of the product will be important factors in developing an industrial process.

Bakelite is a synthetic resin made from formaldehyde and phenol. It was obtained in solid form and was ground to a powder prior to utilization. Four colors have been used; black, red, green, and amber. The powdered resin and milled straw were physically mixed prior to pressing at 350°F.

Acrylic resin was obtained as a ground-up white solid. Physical mixing and pressing at 350°F produced a solid board. The resin becomes transparent as it fuses.

Transoptic Powder, a finely ground solid, initially becomes fluid as it is heated under pressure. Continued heating of a straw/powder mixture produces a solid board. This resin also becomes transparent upon fusion.

Phenol-formaldehyde is one of the resins used in wood particleboard manufacture. It is normally sprayed onto the particles in a water solution. The water is driven off during the heating and pressing cycle when the phenolic compound and the formaldehyde polymerize.

Urea-formaldehyde is also used in wood particleboard manufacture. It is sprayed onto the particles in a water solution. A low pH is needed to trigger the polymerization reaction and since wood contains acid groups it is a very effective resin when used with wood. Since straw appears to be neutral, it may not be as effective without adding an acidic compound.

Polyisocyanate resins are used in conjunction with polyalcohols in the production of polyurethane plastics. It was initially surmised that the cellulose of straw could be utilized as the polyalcohol and that a solid product should result if a polyisocyanate resin were mixed with straw particles and heated under pressure. The term polyisocyanate includes both diisocyanates and polyisocyanates in this report.

Since the polyisocyanate resins are liquid at room temperature, they can be sprayed onto the straw particles. Solvent application is also possible using DCM, acetone, toluene, or benzene.

A list of the resins obtained for straw particleboard formation is provided in Table IV. B. 1.

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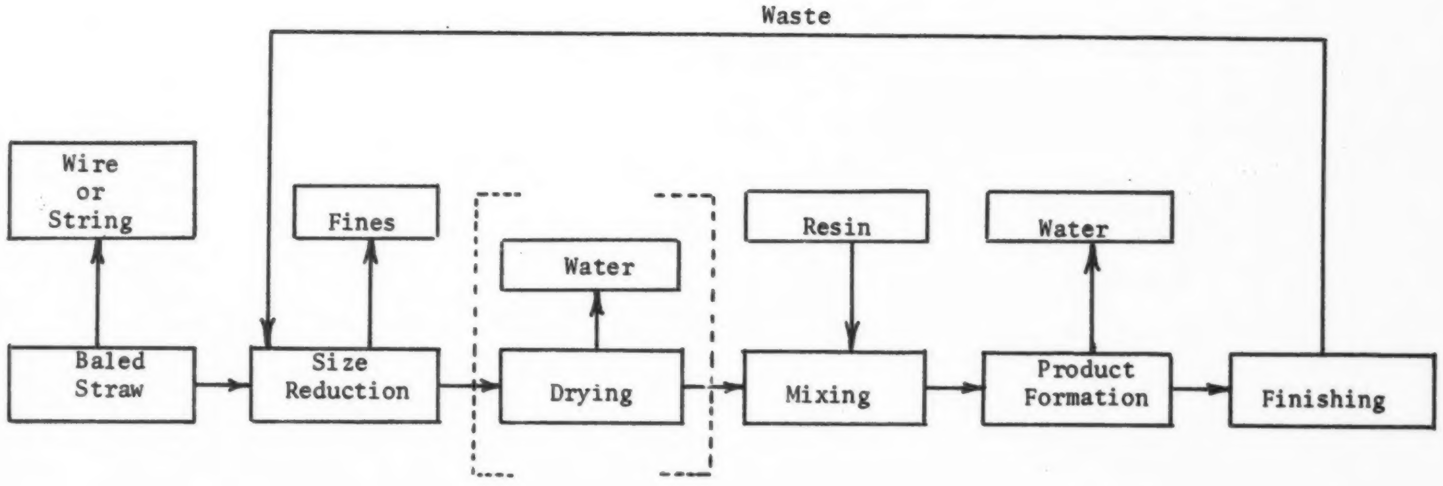
Waste
Wire
or
String
Fines
Water
Resin
Water
Baled
Straw
Size
Reduction
Drying
Mixing
Product
Formation
Finishing

Figure IV. B. 1. Block Diagram Showing the Particleboard Process.

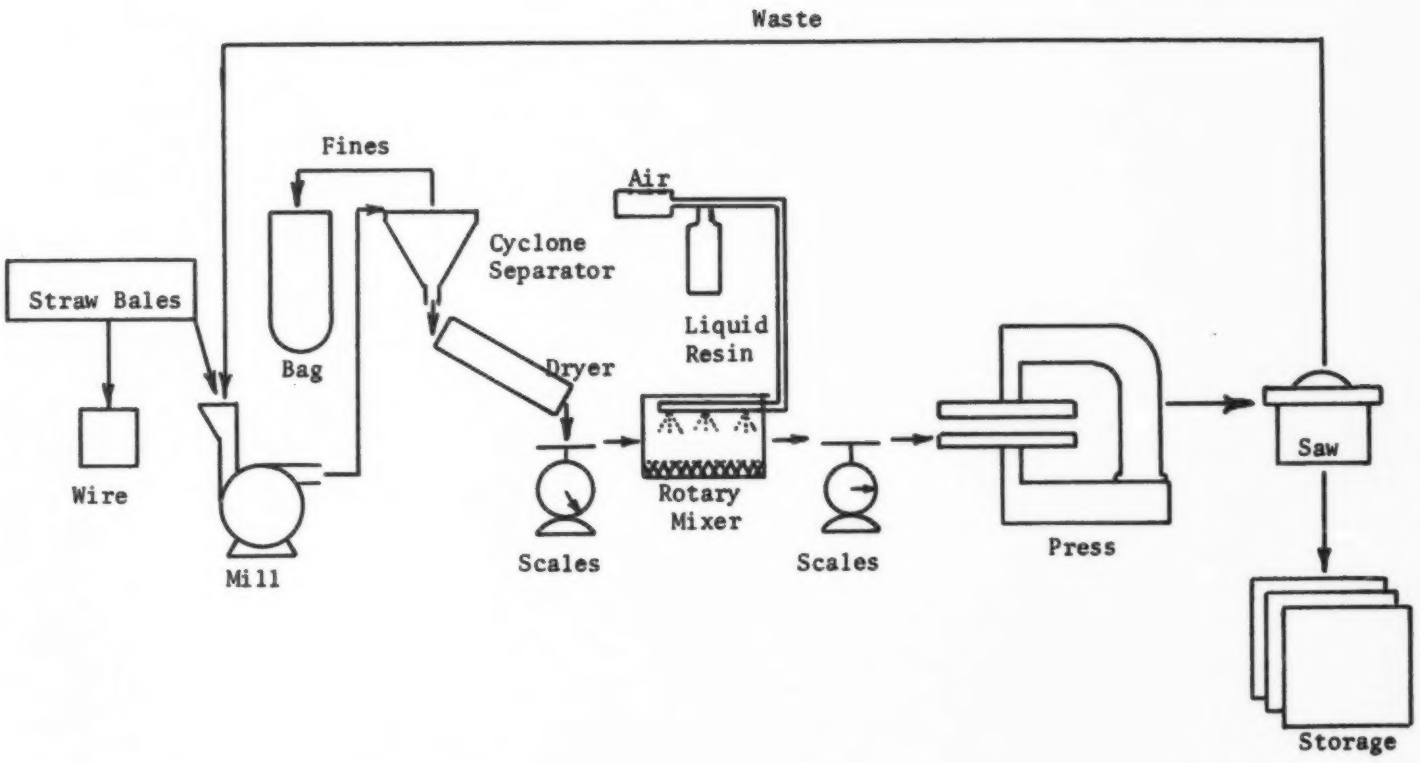
Waste
Fines
Air
Straw Bales
Bag
Cyclone
Separator
Liquid
Resin
Dryer
Wire
Rotary
Mixer
Mill
Scales
Scales
Press
Saw
Storage

Figure IV. B. 2. Schematic Diagram of Straw Particleboard Plant.

Table IV. B. 1. Resins Used in The Laboratory Study of Straw Particleboard

Identification Used In This Report	Chemical Composition	Vendor
Bakelite	Phenol-formaldehyde	Buehler
Acrylic	Polyacrylic esters	duPont
Trans-optic powder		Buehler
PF	Phenol-formaldehyde	Borden
UF	Urea-formaldehyde	Borden
TKI	Tolylene 2,4 diisocyanate	Aldrich
PAPI	Polymethylene polyphenylisocyanate	Upjohn
Isonate 125M	Diphenylmethane diisocyanate	Upjohn
MR	4,4 diphenylmethane diisocyanate	Mobay
MRS	4,4 diphenylmethane diisocyanate	Mobay
	(others available)	
	dianisidine diisocyanate	Carwin
	tolidine diisocyanate	Carwin
	Hexamethylene diisocyanate	Mobay
	m-xylyene diisocyanate	Carwin
	2,4 tolylene diisocyanate	Allied
	4,4' diphenylmethane diisocyanate	duPont

Table IV. B. 2. ESTIMATION OF FIXED-CAPITAL INVESTMENT COST[1]

Dollars

Plant Description: Straw Particleboard - Pilot Plant

Capacity: 100 tons/year product

I. Direct Costs				26,910
A. Equipment			21,510	
1. Purchased Equipment		13,410		
a. Mill w/motor	260			
b. Cyclone separator	40			
c. Dust collector	10			
d. Scale	50			
e. Mixer w/sprayer	5,000			
f. Press	8,000			
g. Saw	50			
2. Installation (35% P.E.)		4,700		
3. Instruments & Controls (6% P.E.)		800		
4. Piping (10% P.E.)		1,300		
5. Electrical (10% P.E.)		1,300		
B. Buildings			5,200	
1. Steel Building 40' x 40' w/concrete pad		4,000		
2. Doors, Windows, etc.		1,200		
C. Service Facilities n/a				
D. Land			200	
II. Indirect Costs				4,570
A. Engr. & Supervision (1/10 of 10% D.C.)			270	
B. Const. & Contractor Fees (10% D.C.)			2,700	
C. Contingency (5% F.C.I.)			1,600	
III. Fixed Capital Investment				31,480
IV. Working Capital (10% T.C.I.)				3,500
V. Total Capital Investment				34,980

[1] Peters, Max S., and Timmerhaus, Klaus D., "Pilot Design and Economics for Chemical Engineers", P. 140, McGraw-Hill, New York, 1968.

Table IV. B. 3. ESTIMATION OF TOTAL PRODUCT COST[1]

Dollars

Plant Description: Straw Particleboard - Pilot Plant

Capacity: 100 tons/year product

I. Manufacturing Cost				27,660
A. Direct Production Costs			23,780	
1. Raw Materials		6,240		
a. Straw ($15.00/ton)	1,740			
b. Resin ($0.45/lb)	4,500			
2. Operating Labor (2 men)		14,000		
3. Supervisory & Clerical (10% of O.L.)		1,400		
4. Utilities		1,400		
a. electricity	1,200			
b. phone	100			
c. water	50			
d. waste disposal	50			
5. Maint., & Repairs (1/10 of 10% F.C.I.)		310		
6. Operating Supplies (0.5% of F.C.I.)		150		
7. Laboratory Charges (1/10 of 20% O.L.)		280		
8. Patents & Royalties (assume none)				
B. Fixed Charges			2,380	
1. Depreciation		1,440		
a. equipment (10% P.E.)	1,340			
b. buildings (2% value)	100			
2. Taxes (2% F.C.I.)		630		
3. Insurance (1% F.C.I.)		310		
4. Rent (n/a)				
C. Plant Overhead (5% T.P.C.)			1,500	
II. General Expenses				3,080
A. Administrative Costs (1/10 of 5% T.P.C.)			180	
B. Distribution and Selling (1/10 of 10% T.P.C.)			300	
C. Research and Development (1/10 of 5% T.P.C.)			150	
D. Financing (7% T.C.I.)			2,450	
III. Total Product Cost				30,740

Unit Cost $\frac{\$30,740}{200,000 \text{ lbs.}} = \$0.15/\text{lb}$

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[1] Peters, Max S., and Timmerhaus, Klaus, D., "Plant Design and Economics for Chemical Engineers", P. 141, McGraw-Hill, New York, 1968.